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THE QUARTERLY JOURNAL OF THE CHEMICAL SOCIETY OF LONDON.

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THE

QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*On Biniodacetic Acid.*

By W. H. Perkin, F.C.S., and B. F. Duppa, Esq.

In the number of "The Philosophical Magazine" for July last we gave an account of the formation and properties of iodacetic acid, which, it will be remembered, was prepared by acting on bromacetic ether with an alcoholic solution of iodide of potassium, the result of which action was iodoccetic ether. This, in its turn, was treated with baryta water, and the resulting barium salt decomposed by sulphuric acid. Since then we have discovered that, by treating bibromacetic ether in a similar manner, biniodacetic acid is formed. We shall now proceed to describe the process we employed for the preparation of this interesting substance from biniodacetic ether, which will be described hereafter.

Biniodacetate of ethyl is decomposed best by shaking it up in a flask with a small quantity of milk of lime, small additions of the latter being made continually until no further smell of the ether can be perceived, or any burning sensation produced on the tongue when a small quantity of the liquid is applied. The mixture of hydrate of calcium and the solution of the new salt is placed on a filter, and well washed—first with cold, and then with hot water—until the liquid, passing through, no longer gives a precipitate of iodide of silver when gently heated with a drop of acid nitrate. The liquid containing biniodacetate and hydrate of calcium and alcohol in solution is then very gently evaporated until it just begins to crystallize. The object of this is to ensure the complete volatilization of the alcohol which was present, as it interferes much with the precipitation of the acid, and has, moreover, a tendency to decompose it. Should any crystals exist in the liquid, a small quantity of water must be added, to bring them in solution. The liquid being cold, dilute hydrochloric acid is added (strong acid decomposes, and also dissolves the acid, as it is separated from its calcium salt)—in sufficient quantity to liberate the acid, and no more. This is known by no further turbidity being produced when more acid is added to a drop on a watch-glass. The milky liquid is now left at rest, when the acid begins to shoot out into a confused mass of crystals. At the bottom of the vessel is generally found a large portion of the acid in the form of a heavy yellow oil, which, after a time, concretes into a mass of large, opaque, sulphur-yellow rhombohedrons. The crystals are repeatedly washed with a little cold water, and dried.

The acid, thus prepared, is a beautifully crystalline sulphur-yellow substance, having a slightly acid and metallic after-taste. It does not act on the skin like the corresponding bromine-compound. It is but slightly soluble in water. Crystals of the acid exposed to the air slowly disappear, being volatile at the common temperature.

On opening a bottle containing crystals of the acid, a faint smell, resembling iodine, manifests itself. Heated on platinum foil, it fuses partly, volatilizes, and then turns black, evolving copious fumes of iodine.

All the salts of this acid we have yet examined are slightly yellow; all crystalline and permanent, with the exception of those of potassium and sodium, which are deliquescent.

Biniodacetate of calcium crystallizes in silky needles of a yellow colour; heated on platinum foil, it evolves iodine.

Biniodacetate of barium is a crystalline salt, forming large rhombohedral crystals of a pale yellow colour, tolerably soluble in water, and giving off iodine when heated. A combustion of a portion, dried in vacuo over sulphuric acid, gave the following results:

·7473 of substance gave
·1605 of carbonic acid and
·0388 of water.

These numbers agree with the formula,

$$Ba,C_4(HI_2)O_4$$

as may be seen by the following table:—

		Theory.		Mean of Experiment.
Carbon	4 equivs. .	24·00	6·32	5·85
Hydrogen	1 „ .	1·00	·26	·57
Barium	1 „ .	68·59	18·07	—
Iodine	2 „ .	253·76	66·86	—
Oxygen	4 „ .	32·00	8·49	—
		379·35	100·00	

Biniodacetate of Lead.—This salt is best prepared by adding a solution of düodacetate of sodium to a solution of acetate of lead, both being largely diluted. After a few moments, the mixture becomes turbid, and a considerable quantity of a crystalline precipitate rapidly forms, which must be well washed with cold water, in which it is nearly insoluble; when dry, it is of a pale yellow colour, and, seen under the microscope, is found to consist of minute prismatic crystals. The following analyses were made:

I. ·5052 of substance gave
·1054 of carbonic acid, and
·0335 of water.

II. ·3695 of substance gave
·0774 of carbonic acid, and
·0200 of water.

III. ·3223 of substance gave
·0675 of carbonic acid, and
·0148 of water.

IV. ·5667 of substance gave
·2035 of sulphate of lead.

Percentage composition:—

	I.	II.	III.	IV.
Carbon . .	5·68	5·71	5·71	—
Hydrogen .	·673	·43	·51	—
Lead . .	—	—	—	24·53

These numbers agree with the formula,

$$Pb,C_4(HI_2)O_4,$$

as may be seen from the subjoined table:—

			Theory.		Mean of Experiments.
Carbon	4 equivs.	.	24·	5·79	5·7
Hydrogen	1 ,,	.	1·	·26	·57
Iodine	2 ,,	.	253·76	61·24	—
Oxygen	4 ,,	.	32·	7·72	—
Lead	1 ,,	.	103·57	24·99	24·53
			414·33	100·00	

Biniodacetate of Silver.—This salt is produced by adding a neutral solution of nitrate of silver to one of düodacetate of sodium. It is best to use dilute solutions, as the precipitate forms more slowly and more perfectly crystallized. The precipitate must be well washed with cold water, and dried in vacuo. It is a yellow crystalline powder, decomposed when gently heated on platinum foil, the decomposition being attended with a slight explosion, one equivalent of iodine being evolved.

This salt, when boiled, readily splits up into iodide of silver and iodoglycolic acid.

The following silver, iodine, and carbon and hydrogen determinations were made:—

I. ·4245 of substance gave
·2350 of iodide of silver.

II. ·8970 of substance gave
·2313 of iodide of silver.

III. ·3350 of substance gave
·3720 of iodide of silver.

IV. .4022 of substance gave
·4510 of iodide of silver, and
·1363 of chloride of silver.

V. ·5430 of substance gave
·1159 of carbonic acid, and
·0148 of water.

Percentage composition:—

		I.	II.	III.	IV.	V.
Carbon .	.	—	—	—	—	5·82
Hydrogen	.	—	—	—	—	·30
Iodine .	.	—	—	59·98	60·57	—
Silver .	.	25·45	25·78	—	25·50	—

These numbers agree with the formula,

$$Ag,C_4(HI_2)O_4$$

as may be seen from the following table :—

		Theory.		Mean of Experiments.
Carbon	4 equivs.	24·00	5·73	5·82
Hydrogen	1 ,,	1·00	·23	·30
Iodine	2 ,,	253·76	60·52	60·27
Silver	1 ,,	108·00	25·78	25·57
Oxygen	4 ,,	32·00	7·74	—
		418·76	100·00	

Biniodacetate of Ethyl.—To prepare this substance, a distilling and condensing apparatus, like that used for the preparation of pure tannin, is convenient, the iodide of potassium being placed in the large tube, and the bibromacetic ether, previously mixed with three times its volume of alcohol, in the flask. The apparatus is then placed on a water-bath, and the contents kept boiling until all the iodide of potassium has dissolved by the constant filtration of the alcohol through it. The iodide should be used in the proportion of two equivalents to one of bibromacetic ether. The flask is then detached, a bent tube fitted to it, and the contents distilled until all the alcohol has passed over, which may be known by the liquid coming over turning milky. The flask is then opened, and a drop of the oily liquid at the bottom tested with a little ammonia, which immediately converts it into the amide, which, when heated with a little oxide of manganese and sulphuric acid, gives off iodine. Should the vapour not be good in colour, and the crystals soft, it is a sign that some bibromacetic ether is still undecomposed, and that the digestion with alcohol must be renewed until the test gives pure-looking iodine vapours. The flask, when the reaction is terminated, is emptied of its contents into a test-glass, and the oil at the bottom taken up with a pipette, and well washed with water. A little mercury is then shaken up with it, when the dark colour of the dissolved iodine will in a few moments vanish.

Thus prepared, biniodacetic ether is a yellowish liquid, having a pungent burning taste, and irritating the eyes and nose in a powerful manner. It is insoluble, or nearly so, in water; ammonia rapidly converts it into biniodacetamide.

We have not made an analysis of this substance, as the reactions we obtained were so clearly definite that we did not consider it necessary.

Biniodacetamide.—As mentioned before, this substance is produced when a solution of ammonia is brought in contact with the above-mentioned ether. It is a difficultly soluble substance, of a pale yellow colour. The following analyses were made:

I. ·5910 substance gave
·1788 of carbonic acid, and
·0593 of water.

II. ·3400 of substance gave
·0995 of carbonic acid, and
·0362 of water.

III. ·5303 of substance gave
·3972 of chloroplatinate of ammonium.

Percentage composition :—

	I.	II.	III.
Carbon . .	8·25	7·98	—
Hydrogen . .	1·11	1·18	—
Nitrogen . .	—	—	4·68

which agree with the formula,

$$C_4(H_3I_2)NO_2,$$

as may be seen by the subjoined table :—

		Theory.		Mean of Experiment.
Carbon	4 equivs. .	24·00	7·72	8·11
Hydrogen	3 ,, .	3·00	·96	1·14
Iodine	2 ,, .	253·76	81·65	—
Nitrogen	1 ,, .	14·00	4·52	4·68
Oxygen	2 ,, .	16·00	5·15	—
		310·76	100·00	

Having experienced great difficulties in making iodine determinations, we beg to be allowed to mention the method we pursued in obtaining the numbers mentioned in this paper.

After having tried all the methods detailed in the manuals, it occurred to us that possibly the iodine might be eliminated from biniodacetic acid by means of nascent hydrogen. The first object to be obtained was the perfect solution of a salt in some liquid without heat. For this purpose we selected the silver salt, mixed it with water, and added a few drops of ammonia, which immediately produced a clear solution. We then added metallic zinc, which directly precipitated the silver in the metallic form, rendering the liquid yellow from a small quantity of iodide of silver that was formed. A few moments' stirring decomposed this, and the liquid became perfectly clear. The metallic zinc and silver were then separated by means of a filter, and repeatedly washed with water, to which a few drops of ammonia had been added, to keep oxide of zinc in solution. The solution was then treated in the ordinary way with nitric acid and nitrate of silver for precipitation of the iodine.

II.—*Description of an hermetically sealed Barometer.*

BY RICHARD ADIE, LIVERPOOL.

WHEN mounted on an ivory scale, this instrument resembles in size and portability a pocket thermometer of the medium or larger class.

It is constructed from a piece of thermometer tube, in which, in lieu of the spherical or cylindrical bulb formed for a thermometer, a cistern is made in the form of the section of a cylinder, 1·4 inches diameter and 1-10th of an inch thick, varying these measures according to circumstances; but generally the bulb has nearly the shape and dimensions of a half-crown. On the top of the tube there is an air cavity similar to that used in Dr. Rutherford's registering thermometer.

A. The cistern containing alcohol.

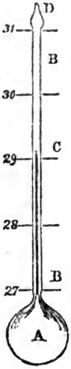
BB. The tube in which the height corresponding to the barometer is read.

C. The top of the alcohol column.

D. The air-cavity for correcting for temperature.

31 to 27. The figures to represent the height of the column C. with reference to the mercurial column.

Sub-divisions between each inch are added so as read off to ·02.



The influence of change of temperature is got rid of by trial and adjustment of each instrument; so that the expansion of the air in the upper cavity will counterbalance the expansion of the liquid in the cistern. This correction for temperature applies only to the condition of equal heating of the instrument throughout. When it is well done, an instrument is obtained, which is extremely sensitive to any change of atmospherical pressure.

If dipped in water at the temperature of the air, the column in the tube immediately rises to show the increase of pressure. When carried from one story of a house to another, the change is noticed as the stairs are ascended. In the beginning of last April, I put one of the barometers in the corner of the compartment of the railway carriage in which I was travelling, from Liverpool to Edinburgh, where it indicated regularly the extensive changes from the sea level which that line of route contains.

The hermetically-sealed barometer which I have found to work best is filled with coloured alcohol; the column in the tube moving through about 1·5 inches for every inch of the mercurial barometer.

Filled with mercury, instruments corrected for temperature were obtained to move through half an inch for every inch of the barometer; but, in point of mobility, they were much inferior to alcohol-filled tubes.

Filled with ether, an instrument corrected for temperature could not be obtained in combination with delicacy of indication; but if the correction for temperature be dispensed with, and a place can be found for the barometer where the changes of temperature are small, ether, in an hermetically-sealed tube of the kind described, would furnish a most minute measure of changes in atmospheric pressure.

A tube filled with water did not act with delicacy, from the want of mobility in the fluid.

In the hermetically sealed barometer, the reading may be much disturbed by unequal heating, when the instrument is held in the hand, or the sun allowed to shine on a portion of it. This can in a degree be prevented by the skill of the observer, with the interposition of non-conductors, and when carried by holding the instrument suspended by a cord, rather than keeping it in the pocket or hand. When the indication has been disturbed by unequal heating, it must remain suspended fifteen or twenty minutes before a reliable reading can be made.

III.—*Action of Pentachloride of Phosphorus on Tartaric Acid.*

By W. H. Perkin, F.C.S. and B. F. Duppa, Esq.

In a paper on malic acid, published last April in the Philosophical Magazine, we mentioned that we were engaged with the study of the influence of pentachloride of phosphorus on Tartaric acid; our time, however, having been much occupied by other subjects, we have as yet been unable to investigate the matter thoroughly, but, having obtained some peculiar results, we take this opportunity of laying them before the Society.

On gently heating a mixture of pentachloride of phosphorus and tartaric acid, hydrochloric acid is evolved in abundance, and a perfectly liquid mixture is formed consisting of oxychloride of phosphorus and an oil. To obtain the latter in quantity we have found it best to operate in the following manner.

One part of pulverized tartaric acid and five or six of pentachloride of phosphorus are mixed and introduced into a retort and gradually heated until perfectly liquid. The temperature is then elevated and the liquid allowed to distil until it reaches 120°; it is maintained at this point, and dry air passed through the remaining liquid for five or ten minutes, so as to separate as much of the remaining oxychloride of phosphorus as possible.

This product, which is the chloride of a diatomic acid radical, sinks as an oil, when thrown in water, and gradually dissolves. It also dissolves in alcohol, forming an ethereal body. If projected into strong aqueous ammonia, a violent action ensues, chloride of ammonia and a new crystalline compound, very soluble in alcohol and water, being produced. With phenylamine this body reacts most energetically. It decomposes partially on being distilled.

As mentioned above, this substance gradually dissolves in water. If a considerable quantity is mixed with water, it becomes warm, and, on cooling, deposits a white, slightly crystalline acid. If exposed to the moist atmosphere for a day or two, it becomes a white solid mass.

This acid, after being well pressed between bibulous paper and recrystallized from water, presents itself as a white, almost amorphous, mass: but, when viewed under the microscope, appears as small transparent needles. It is very soluble in water and alcohol, has a very acid taste, melts when heated, and solidifies into a crystalline mass on cooling. It is bibasic.

Acid potassium-salt. This is best obtained by taking a solution of the acid and dividing it into two equal portions, neutralizing one with carbonate of potassium and then adding the other to it. If not too dilute, the new salt immediately makes its appearance as a crystalline precipitate, which, after washing with cold water and recrystallizing once or twice, is obtained quite pure. It crystallizes in plates. It is more soluble than the acid tartarate of potassium. It contains chlorine. The following carbon, hydrogen, chlorine, and potassium determinations have been made:

I. ·3290 of substance gave
·3033 of carbonic acid, and
·0329 of water.

II. ·2064 of substance gave
·1567 of chloride of silver.

III. ·69525 of substance gave
·271 of chloride of potassium.

Percentage composition:—

Carbon	25·14
Hydrogen	1·11
Chlorine	18·82
Potassium	20·45

which agrees with the formula $KH,C_8(HCl)O_8$ as may be seen from the following table:—

		Theory.		Exp.
Carbon	8 equiv.	48	25·4	25·14
Hydrogen	2 „	2	1·05	1·11
Chlorine	1 „	35·5	18·81	18·82
Potassium	1 „	39·2	20·77	20·45
Oxygen	8 „	64·0	33·97	
		188·7	100·00	

The *neutral potassium-salt* is crystalline, and much more soluble than the former.

Silver-salt.—On adding nitrate of silver to a solution of either of the above salts, a white precipitate is immediately formed, this, when washed with cold water and dried in vacuo over sulphuric acid is fit for analysis. It is very slightly soluble in water. When viewed under a powerful lens, it presents a slightly crystalline appearance. On being heated on platinum foil, it decrepitates, leaving a residue of metallic silver and chloride of silver. The subjoined determinations were made :—

I. ·2655 of substance gave
·210 of chloride of silver.

II. ·29325 of substance gave
·17375 of metallic silver, and
·117 of chloride of silver.

Percentage composition :—

	I.	II.
Silver	59·5	59 25
Chlorine	——	9·50

These numbers agree with the formula $Ag_2,C_8(HCl)O_8$ as may be seen from the following table :—

		Theory.		Exp.
Carbon	8 equiv.	48	13·16	——
Hydrogen	1 ,,	1	·27	——
Chlorine	1 ,,	35·5	9·74	9·50
Silver	2 ,,	216·0	59·23	59 37
Oxygen	8 ,,	64·0	17·60	——
		364·5	100·00	

Lead-salt. This salt is obtained by adding acetate of lead to a solution of the potassium salt. It is a crystalline substance difficultly soluble in water.

From the foregoing it evidently appears that the new acid has the composition $C_8(H_3Cl)O_8$, and the chloride from which it is derived, the formula $C_8(HCl)O_4,Cl_2$. This acid in composition represents maleic or fumaric acid, in which one equivalent of hydrogen is replaced by chlorine; but, as it is a very soluble substance, it would appear that if derived from either of the above, it would be from maleic acid, therefore we give it the provisional name of *chloromaleic acid.* We hope shortly to be able to replace the chlorine in this acid by hydrogen, and then to ascertain whether it might be viewed as a derivative of maleic acid or not, because this is important, as it may show us the relation which tartaric acid bears to malic.

The action of pentachloride of phosphorus may be explained thus:—

$$\underset{\text{Tartaric acid.}}{\underline{C_8H_6O_{12}}} + PCl_5 = \underset{\text{Anhyd. tart. acid.}}{\underline{C_8H_4O_{10}}} + PCl_3O_2 + 2HCl.$$

Then—

$$C_8H_4O_{10} + 3PCl_5 = \underset{\text{New chloride.}}{\underline{C_8(HCl)O_4,Cl_2}} + 3PCl_3O_2 + 3HCl.$$

This appears to show that tartaric acid represents four molecules of water and that part of the hydrogen and oxygen exist in the same peculiar condition as in glycolic and lactic acid.

The formula of tartaric acid appears to be $\left.\begin{matrix} C_8H_2O_4 \\ H_4 \end{matrix}\right\} O_8$

We have obtained some very interesting substances by digesting the bromacetic ethers with sulphocyanides, acetates, succinates, &c., the study of which we are now engaged with.

IV.—*On the Application of Electrolysis to the Detection of the Poisonous Metals in Mixtures containing Organic Matters.*

By Charles L. Bloxam.

Every analyst is only too well aware of the difficulties which beset the detection of the poisonous metals in mixtures containing organic matters, such as the contents of the stomach, the solids and fluids of the body, and articles of food.

The process which, I believe, most chemists now generally adopt in such cases, consists in disintegrating and partly oxidising the organic matters, by the aid of a mixture of hydrochloric acid and chlorate of potassa, and afterwards precipitating the filtered solution by hydrosulphuric acid, the arsenic acid having been previously reduced by means of sulphurous acid.

In most cases, the solution obtained by treating the organic matters with hydrochloric acid and chlorate of potassa affords a precipitate on the passage of hydrosulphuric acid, whether any of the metals forming insoluble sulphides be present or not: this precipitate is generally of a dark greyish brown colour; is very difficult to filter and wash; and interferes in a most disagreeable manner with the application of the tests for those metals which are precipitable by hydrosulphuric acid from their acid solutions.

It is therefore in the highest degree desirable to adopt some more satisfactory method for separating the metals of the hydrosulphuric acid group from organic mixtures.

Two of these metals, arsenic and antimony, may, it is true, be readily extracted in the form of gaseous hydrogen compounds, by Marsh's process; and the objections to this course have been so often commented on, that, when I repeat some of the most important of them here, it is only that I may plead a fair excuse for submitting this communication to the society.

The occasional presence of arsenic in the sulphuric acid, and of both arsenic and antimony in the zinc, has always been a serious objection to the use of Marsh's test; and although the hydrogen evolved at the beginning of the experiment may be carefully examined before introducing the suspected liquid, the operator always proceeds upon the assumption that the zinc is perfectly homogeneous, and that it is impossible for arsenic or antimony, which had eluded detection in the first portion of hydrogen evolved, to become apparent when the mass of the zinc has entered into solution.

When liquids holding organic matters in solution are introduced into Marsh's apparatus, the frothing occasioned by the viscidity of the mixture often gives rise to very serious inconvenience; for although it may generally be checked by the addition of alcohol, it sometimes gets quite beyond the control of the operator, and the experiment is entirely lost.

But the most serious objection is that the liquid which has been examined by this method for arsenic and antimony cannot be examined for any other metals, on account of the presence of so large a quantity of sulphate of zinc, a consideration of very grave importance in cases where the quantity of the suspected matter is small.

The objections to the convenient and delicate process of Reinsch rest upon similar grounds, and are even more readily admissible.

The detection of the poisonous metals by the decomposing action of the galvanic current, is, I think, free from these objections, and so minute quantities of the poisonous metals may be detected by this method of testing, that it may safely be relied upon in most cases of chemico-legal investigations.*

The first experiments were directed to ascertain whether minute quantities of the most important poisonous metals could be easily detected, by electrolysis, in solutions free from organic matters.

Detection of Arsenic.

The apparatus which was at first employed, consisted of an ordinary U-tube, one limb of which was closed with a perforated cork through which passed a tube for the escape of the hydrogen, and a platinum wire connected with the zinc extremity of a Grove's battery of five cells; to this wire was attached a platinum plate, measuring about 2 inches by ¾ inch, which was thrust down almost to the bottom of the U-tube. The other limb of this tube was left open for the escape of the oxygen, and contained a similar platinum plate, connected with the platinum extremity of the battery.

The tube which carried off the hydrogen was connected with a straight tube of hard glass drawn out to a long open point, and heated to redness at the shoulder in order that any arseniuretted hydrogen might be decomposed in passing through it.

At the commencement of each experiment, the U-tube was charged with a fluid ounce of diluted sulphuric acid (containing one measure of oil of vitriol and four measures of water), and as soon as the closed limb had become filled with hydrogen, the drawn-out tube was heated with a spirit-lamp for 15 minutes in order to ascertain that no deposit of arsenic was obtained from the sulphuric acid alone. The solution to be examined for arsenic was then introduced into the closed limb, by withdrawing the cork for an instant, and the experiment continued.

The U-tube was immersed in a vessel of water to prevent the temperature from rising too high during the passage of the current.

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* Before submitting this communication to the Society, the author was not aware of the existence of M. Gaultier de Claubry's admirable paper upon this method (J. Pharm. [3], xviii, 125; *abstr.* Chem. Soc. Qu. J. iii, 162). This chemist, however, appears to have relied upon the precipitation of the arsenic, not upon its evolution in the form of arseniuretted hydrogen.

The quantity of arsenic employed for each experiment was determined by carefully measuring out a standard solution of arsenious acid.

Three experiments made with aqueous solutions containing $\frac{1}{10}$, $\frac{1}{100}$ and $\frac{1}{1000}$ grain, respectively (corresponding to ·076, ·0076 and ·00076 grain of metallic arsenic), proved that the arsenic could be readily obtained, as in Marsh's test, in the form of a brilliant metallic crust in the narrow point of the tube, about half an inch beyond the heated portion.

In order to ascertain whether the presence of alcohol would interfere with the action of the test, in case it might become necessary to add it in order to prevent frothing, an ounce of dilute sulphuric acid and a drachm of alcohol were introduced into the apparatus and electrolysed until the tubes were full of hydrogen; on heating the evolution tube, a faint odour resembling mercaptan was perceived, but there was not the slightest deposit. On introducing $\frac{1}{100}$ grn. of arsenious acid, a most satisfactory mirror was formed in the tube in less than five minutes, and a decidedly arsenical odour, like that of alkarsin, proceeded from the extremity of the evolution tube.

In subsequent experiments, as in this, I found that the presence of alcohol appeared to facilitate the production of an arsenical crust, and that the arsenical odour afforded a valuable confirmation with respect to the presence of arsenic.

The method was then tested as to its applicability in cases where the arsenious acid is mixed with large quantities of organic matters.

A mixture was prepared, containing about 1 oz. lean meat, 1 oz. bread, 1½ oz. milk and ½ oz. white of egg, beaten to a pretty uniform pulp in a mortar. To this mixture was added an aqueous solution of $\frac{1}{10}$ grain of arsenious acid. The whole was then mixed with 1 fluid oz. of hydrochloric acid and 4 oz. of water; this mixture was digested in the water-bath for 15 minutes, filtered, and the clear solution evaporated on the water-bath to 3¼ fluid oz. of a dark brown viscid liquid.

On introducing one-fourth of this (= 0·025 grn. AsO_3) into the decomposing tube, it frothed up very much, but was immediately checked by the addition of a drachm of alcohol, and a deposit of arsenic was almost immediately formed in the heated tube.

A repetition of the experiment gave a similar result, but about 15 minutes were required for the formation of a good arsenical mirror.

In a third trial, one-sixth of the solution was taken (=0·017 grn. AsO_3), with a like result, the odour of alkarsin being also very distinct.

A fresh organic mixture was poisoned, as before, with $\frac{1}{10}$ grn. of arsenious acid, and treated in the same manner, being finally evaporated to 2 fluid oz.

One-tenth of this opaque brown liquid (=0·01 grn. AsO_3) gave a very distinct mirror in less than 5 minutes, attended with a strong arsenical odour.

One-hundredth of this liquid (= 0·001 grn. AsO_3) also gave a very distinct mirror and odour in 10 minutes.

Since arsenic is sometimes contained in organic mixtures in a form (*e. g.* that of sulphide of arsenic) not readily soluble in hydrochloric acid, it became necessary to ascertain whether the solution obtained by adding chlorate of potassa together with the acid, would give the indication of arsenic by this method of testing: for such a solution would of course contain the arsenic in the form of arsenic acid.

The experiments made to determine this point proved that small quantities of arsenious acid ($\frac{1}{20}$ grn.) could not be detected by this test after boiling with hydrochloric acid and chlorate of potassa, unless the solution had been digested with sulphurous acid in order to reduce the arsenic acid.

The behaviour of tersulphide of arsenic was then examined.

One-tenth grn. of arsenious acid was precipitated as sulphide, the latter dissolved in hydrochloric acid and chlorate of potassa, and the solution evaporated on the water-bath till the odour of chlorine was no longer perceptible. One-half of this liquid (= 0·05 grn. AsO_3) was introduced into the decomposing tube, but no indication of arsenic was obtained in 15 minutes.

The other half was saturated with sulphurous acid gas, digested for some time in the water-bath, and evaporated till the odour of sulphurous acid had disappeared. On subjecting it to the electrolytic test, a distinct mirror of arsenic was obtained in 10 minutes.

One-tenth grn. of tersulphide of arsenic (= 0·06 grn. As) dissolved in diluted sulphide of ammonium was added to a mixture of articles of food similar to that previously used, with the addition of $\frac{1}{2}$ oz. of strong ale.

The mixture was digested on a water-bath with 1 oz. of hydrochloric acid and 3 oz. of water, chlorate of potassa being added in small quantities until a thin homogeneous fluid was obtained; the filtered liquid was digested for half an hour with a large excess of a saturated solution of sulphurous acid, then evaporated on the water-bath to about 1¼ oz.

One half of this very nasty brown syrupy liquid was mixed with a drachm of alcohol and introduced into the decomposing cell. The want of mobility in the liquid somewhat retarded the evolution of gas, but in less than 15 minutes, the arsenical deposit commenced, and in 30 minutes, a very beautiful mirror was obtained.

In one or two of the experiments with organic mixtures, minute quantities of arsenic had escaped detection without any assignable cause; and I was therefore led to make some experiments to ascertain whether any influence was exerted by a variation in the amount of hydrochloric acid present in the solution.

A standard solution was prepared by dissolving 1 grn. of arsenious acid, in 1000 grns. (by measure) of hydrochloric acid.

10 grns. of this solution ($\frac{1}{100}$ grn. AsO_3), mixed with 20 grns. of hydrochloric acid, gave a very distinct crystalline deposit of arsenious acid in the tube, but no sublimate of metallic arsenic, although a deposit of arsenic was formed upon the negative plate. 100 grns. of the solution ($\frac{1}{10}$ grn. AsO_3) mixed with 200 grns. of hydrochloric acid, gave a similar result. 50 grns. of the solution ($\frac{1}{20}$ grn. AsO_3), diluted with 400 grns. of water, behaved in the same way.

In these cases, the arseniuretted hydrogen appeared to have been converted into terchloride of arsenic, which was decomposed by the aqueous vapour on passing the heated portion of the tube, with formation of arsenious acid.

Finding that, in these experiments, the smell of chlorine was distinctly perceptible at the end of the evolution tube, and believing that the chlorine disengaged at the positive plate, diffusing itself through the liquid, caused the decomposition of the arseniuretted hydrogen, I employed another apparatus, consisting of two decomposing cells, separated by a diaphragm of vegetable parchment.

In this form of apparatus, 10 grns. of the solution of arsenious acid in hydrochloric acid (= $\frac{1}{100}$ grn. AsO_3), mixed with 120 grns. of hydrochloric acid, and introduced into the negative cell of the apparatus (the latter having been charged, as usual, with a fluid ounce of dilute sulphuric acid), gave a beautiful mirror of arsenic in two minutes.

A mixture of articles of food, to which $\frac{1}{100}$ grn. of arsenious acid had been added, was digested with a fluid ounce of hydrochloric acid, and three or four ounces of water; the filtered solution was evaporated down to one ounce upon the water-bath, and one-tenth of it (= $\frac{1}{1000}$ grn. AsO_3), was introduced into the apparatus with ½ drm. alcohol. In less than fifteen minutes, a very distinct arsenical mirror had been formed.

The apparatus which was ultimately found most suitable for the detection of arsenic by electrolysis, consisted of a two-ounce narrow-mouthed bottle, the bottom of which had been cut off, and replaced by a piece of vegetable parchment tightly stretched over it and secured by a ligature of thin platinum wire (even vulcanised caoutchone is speedily corroded). The bottle was furnished with a cork, carrying a small tube, bent at right angles, and connected with the drawn-out reduction tube by a caoutchouc tube; through this cork passed a platinum wire bent into a hook, inside the bottle, for suspending the negative plate. The bottle was placed in a glass of such a size, as to leave a small interval between the two, and this glass was allowed to stand in a large vessel of cold water; an ounce of dilute sulphuric acid was introduced into the apparatus, so as to fill the bottle and the outer space to about the same level, the positive plate being immersed in the acid contained in this outer space. When the bottle had become filled with hydrogen, the shoulder of the reduction tube was heated to redness during fifteen minutes, to ascertain the purity of the sulphuric acid, and the liquid to be tested was introduced into the bottle, by means of a pipette, the cork being removed for an instant; a drachm of alcohol was afterwards introduced by the pipette to prevent frothing.

In the following cases, the arsenic was most satisfactorily detected in this apparatus, the evidence of its presence being threefold, and resting, firstly, upon the formation of the characteristic arsenical mirror; secondly, upon that of a small shining ring of crystalline arsenious acid, slightly in advance of the mirror; and thirdly, upon the development of the peculiar alliaceous odour.

$\frac{1}{1000}$ grn. arsenious acid in hydrochloric solution.
$\frac{1}{10000}$,, ,, aqueous solution.
$\frac{1}{100}$,, dissolved in 120 grns. hydrochloric acid.
$\frac{1}{200}$,, ,, 115 ,, ,,
$\frac{1}{1000}$,, ,, 120 ,, ,, and 240 grns. water.

These experiments were repeated with the same results.

Experiments were then made upon organic mixtures containing arsenic, which were boiled with hydrochloric acid and chlorate of potassa, the arsenic acid being afterwards reduced to the arsenious, by digesting with sulphurous acid, or better with a few drops of a strong solution of bisulphite of soda.

By this process, $\frac{1}{100}$ grn., and even $\frac{1}{1000}$ grn. of arsenious acid, could be detected in an organic mixture with the greatest ease and certainty.

If the sulphurous acid be not entirely expelled after the reduction, a little tersulphide of arsenic is deposited in advance of the metallic crust.

The following process appeared to me the most trustworthy, for the detection of minute quantities of arsenic in articles of food.

The solid matters are reduced to a pretty fine state of division, mixed with enough water to form a thick gruel, and digested, in a a dish placed on a water-bath, with about $\frac{1}{2}$ oz. of hydrochloric acid, for an hour, powdered chlorate of potassa being occasionally added, as directed by Fresenius and von Babo, until the organic matters are disintegrated, when the liquid is filtered off, and evaporated to about an ounce upon the water-bath. The brown fluid thus obtained, is poured into a flask, and a few drops of a strong solution of bisulphite of soda are added to it, until it smells strongly of sulphurous acid; the flask is then heated in a water-bath, until this odour has disappeared, when the solution is mixed with at least an equal volume of water, and introduced into the apparatus arranged and charged as above, a little alcohol being poured upon the top. The operation should be continued for half an hour before the absence of arsenic is inferred.

The advantages which appear to me to belong to this mode of testing, are, that it involves the use of a metal which has never been known to contain arsenic; that the very same portion of sulphuric acid which is employed throughout may be subjected to the test for any length of time, before the suspected liquid is introduced; that the evolution of gas is uniform throughout the experiment, and is always so slow, that no dread of losing the arsenic need assail the mind of the operator; that the experiment may be interrupted for any length of time, by breaking the contact with the battery, without the least injury; that the foulest liquids can be as readily tested as those which are perfectly clear;

and that the same portion may afterwards be further tested by any other process.

The importance of this last consideration was fully exemplified in some of the early failures, before I was well acquainted with the test, for I always succeeded in detecting the arsenic in the same portion of the liquid by Marsh's test.

It is evident, moreover, that this operation enables us to detect minute quantities of copper, antimony, mercury and bismuth, if they be present in the solution.

On considering the detection of the other poisonous metals in this way, it is obvious that lead must be altogether excepted, on account of the insolubility of its sulphate. Silver must also be omitted, where hydrochloric acid is the solvent; and baryta, of course, would not be expected to answer. The remaining important poisonous metals, antimony, copper, mercury, bismuth and zinc, were therefore tried, bismuth being included, on account of the medicinal use of its compounds.

Detection of Antimony.

1 grn. of tartar-emetic (= 0·36 grn. Sb) dissolved in water, was introduced into the decomposing cell. A mirror of antimony was formed, just at each margin of the flame which heated the reduction tube, and a copious deposit of antimony was formed on the negative plate.

$\frac{1}{10}$ grn. of tartar-emetic (= 0·036 grn. Sb), gave only a slight white incrustation, and no mirror, in the reduction tube. The black deposit of antimony on the negative plate was dissolved by heating the latter with a few drops of yellow sulphide of ammonium; on decomposing this solution with acetic acid, a very distinct orange precipitate of tersulphide of antimony was obtained. A mixture of articles of food was mixed with $\frac{1}{10}$ grn. of tartar-emetic, and treated exactly according to the process above described for the detection of arsenic. There was no appearance of a metallic deposit in the reduction tube in twenty minutes; but there was a thick coating of antimony upon the negative plate, which was dissolved by yellow sulphide of ammonium. A portion of this solution, when evaporated in a watch-glass on the water-bath, left a residue having a decided orange colour.

A second and even a third coating of antimony was obtained, by again immersing the plate for a few minutes, and when the film was very slight, it was at once identified by the orange stain produced, when a drop of sulphide of ammonium was evaporated upon it.

The result of the two last experiments, which was fully confirmed in all subsequent trials, is a very important one, as showing that minute quantities of antimony are not nearly so likely to be mistaken, even for a time, for arsenic, in the electrolytic, as in Marsh's test, and this seems attributable to the superior electro-positive tendency of antimony, which disposes it to precipitate more readily upon the negative plate. In no case have I failed to detect antimony in this way.

The following mode of proceeding may be recommended for the detection of the poisonous metals by electrolysis:—

The mixture, which may, of course, have been previously examined for organic poisons, by the usual methods, is digested, on a water-bath, with so much water, hydrochloric acid, and chlorate of potassa, as may be required to disintegrate the solid portions, and to render the liquid capable of filtration; the filtrate is evaporated on the water-bath to a small bulk, and digested in a flask with a sufficient quantity of solution of bisulphite of soda to impart a strong odour of sulphurous acid. The solution is heated in the water-bath until the odour has disappeared, and is once more concentrated, if necessary, by evaporation. It is then diluted with a volume of water, equal to *at least* twice that of the hydrochloric acid present, and introduced into the decomposing cell, enough alcohol being poured upon it to prevent any inconvenient frothing. The passage of the current having been continued for about an hour, the negative plate is withdrawn, washed, and boiled in somewhat dilute yellow sulphide of ammonium for a minute or two. This solution is then evaporated in a watch-glass, placed on the water-bath, and the orange residue of sulphide of antimony identified by the usual tests. The platinum plate having been again washed, is boiled in a few drops of concentrated nitric acid, to which a drop of dilute hydrochloric acid should be added, to dissolve the sulphide of mercury. The acid solution is boiled down in the test tube to a small bulk, and mixed with an excess of ammonia, when the presence of copper will be rendered evident, and the teroxide of bismuth will be precipitated, together with a little ammonio-chloride of platinum. This precipitate when dissolved in hydrochloric acid, evaporated, and largely diluted, will present the indication of bismuth. The filtered ammoniacal liquid, acidulated with hydrochloric acid, and boiled with clean copper, affords the usual evidence of the presence of mercury.

Of the metals above mentioned, mercury was found to be the only one which interferes with the detection of arsenic.

If this metal be detected, the liquid taken from the decomposing cell (or a fresh portion of the original hydrochloric solution), may be distilled, according to Dr. Odling's recommendation, in order to separate the arsenic from the mercury.

The residue may still, if the analyst deem it expedient, be further dealt with by incineration or otherwise, for the detection of other metals.

V.—*On the Composition of Air from Mont Blanc.*

By Dr. E. Frankland, F.R.S.

The greatly increased perfection of gasometric analysis and the numerous minute investigations made by Regnault, Bunsen and others during the past ten or fifteen years, have rendered our knowledge of the composition of atmospheric air exceedingly complete, as far at least as its two chief constituents are concerned. The earliest analyses of air led chemists to believe that the relative proportions of these constituents were liable to very considerable fluctuations. As the processes employed, however, became more accurate, these discrepancies gradually disappeared; until, at length, carefully conducted experiments showed an apparent uniformity in the composition of samples of air taken from the most widely different localities; but it remained for subsequent and far more delicate methods of research to demonstrate that, notwithstanding these apparently accordant results, the composition of the atmosphere does in reality exhibit certain fluctuations, confined, however, within very narrow limits.

The first series of experiments belonging to the latter category, and which may be said to have first established the variability of the percentage of atmospheric oxygen, are those of Bunsen, made upon samples of air collected at Marburg on ten different days, and exhibiting, when freed from carbonic acid, a percentage of oxygen varying from 20·973 to 20·840, whilst no two analyses of the same sample differed more than ·031 per cent. from each other.

Then followed a most elaborate series of determinations by **Regnault**, begun in December, 1847, upon the air of Paris, and continued in January, 1848. The variations in the percentage of oxygen here observed were, in December, 1847, from 20·90 to 21·00, and in January, 1848, from 20·89 to 20·99.

Lewy collected air near the surface of the sea, on the 18th December, 1847, at 3 P.M., in lat. 21° 9′ N. and long. 42° 52′ W. of Paris, temperature 24° C. and found it to contain:—

Nitrogen . . .	78·886
Oxygen . . .	21·060
Carbonic Acid . .	·054
	100·000

Another specimen collected December 4th, 1847, at 3 A.M. in lat. 47° N. and long. 13° W., temperature 13° C. contained:—

Nitrogen . . .	79·006
Oxygen . . .	20·961
Carbonic Acid . .	·033
	100·000

A large number of analyses by the same chemist demonstrate that the air near the surface of the sea contains about the same proportion of carbonic acid as that resting upon the land, and that the sea air is richer, both in oxygen and carbonic acid by day than by night; a fact which he explains by assuming that dissolved air is liberated during the day from the heated surface-layer of the ocean, such dissolved air being, as is well-known, much richer than atmospheric air in the two gases just named. **Lewy** also made a very extended series of analyses of air collected at New Granada and Bogota, during the dry and rainy seasons. The mean of eleven analyses of air from New Granada gave:—

Nitrogen . . .	78·946
Oxygen . . .	21·014
Carbonic Acid . .	·040
	100·000

Analyses of air from Bogota collected during the dry and rainy seasons gave the following mean numbers:—

	Dry Season.	Rainy Season.
Nitrogen . .	78·932	78·966
Oxygen. . .	21·022	20·996
Carbonic Acid .	·046	·038
	100·000	100·000

On some occasions, the air of New Grenada was found to contain as much as 0·49 per cent. of carbonic acid, on which occasions the percentage of oxygen fell as low as 20·331. This abnormal composition is ascribed to volcanic eruptions and extensive conflagrations. In nearly all cases, Lewy seems to have found that an increased amount of carbonic acid in the air was accompanied by an increase in the percentage of oxygen.

Messrs. H. and A. Schlagintweit determined, by weighing, the amount of carbonic acid in the air at great elevations in the Eastern Alps by absorption with potash; but as the increase in weight of the potash apparatus was only from 3 to 6 milligrammes in each experiment, and as the two weighings were made at intervals of nearly two months, these determinations can only be regarded as approximative. Messrs. Schlagintweit found the volume of carbonic acid to vary from ·032 to ·058 per cent. Up to an altitude of 11,043 feet, they found a gradual increase of carbonic acid, but at this elevation they conceived that a constant maximum was arrived at. In some later experiments on the air of Monte Rosa, at heights varying from 13,374 to 13,858 feet, the same experimenters found a mean percentage of carbonic acid equal to ·079 and a maximum of ·095.

In the year 1852, M. Regnault published an extensive series of determinations of the percentage of oxygen in samples of air, deprived of carbonic acid, from different localities. The following is a condensed summary of his results :

				Percentage of Oxygen.	
100	specimens	from	Paris and neighbourhood (1848	20·913	20·999
9	,,	,,	Lyons, Montpellier & St. Martin-aux-Arbres	20·918	20·966
30	,,	,,	Berlin (1848 & 1849)	20·908	20·998
10	,,	,,	Madrid (1848)	20·916	20·982
23	,,	,,	Geneva, Mont Salêve and Mont Buet	20·909	20·993
15	,,	,,	Toulon, the Mediterranean and Algiers	20·912	20·982
5	,,	taken	during a voyage from Liverpool to Vera-Cruz	20·918	20·965
1	,,	from	Guallalamba, South America	20·960	
2	,,	,,	the summit of Pichincha (15,924 feet)	20·949	20·988

In this investigation, a few remarkable deviations from these normal amounts of oxygen were observed, viz. :—

	Percentage of Oxygen.	
Air collected in the Harbour of Algiers, June 5th, 1851	20·42	20·395
Air from Bay of Bengal, February 1st, 1849	20·46	20·45
Air from Ganges, March 8th, 1849. Temperature 35° C., foggy weather, much decomposing organic matter in the water. Commencement of an outbreak of cholera	20·390	20·387

It would be interesting to know how far these results were really abnormal, as regards the relative proportions of oxygen and nitrogen, since it is not improbable that the apparently small percentage of oxygen indicated, was in reality due to the presence of gaseous organic matters in larger quantity than usual ; the ignition of these with excess of hydrogen, in the mode adopted in these analyses would have the effect of converting the carbon of such organic matters into carbonic oxide, thus diminishing the contraction of volume on explosion and consequently the apparent percentage of oxygen. Should such abnormal specimens of air be again encountered, it would be desirable, subsequently to the analysis made in the usual manner, to ignite other portions of them with an equal volume of mixed electrolytic gases, so as to convert the carbon of any organic matter that might be present into carbonic acid which could then be estimated in the usual manner by absorption with potash.

Dr. Miller examined air collected during a balloon ascent in August, 1852, at a height of 18,000 feet, and also a sample collected near the surface of the earth at the same time, with the following results:

	Air from altitude of 18,000 feet.	Air near the earth.
Percentage of Oxygen . .	20·88	20·92

After these numerous and minute analyses, establishing as they do, with few exceptions, the slight, but still undoubted, variations in the relative proportions of the two chief atmospheric gases, any further contributions to this particular branch of our knowledge can only be of comparatively small value. Nevertheless, as an apportunity was afforded me for collecting specimens of air whilst accompanying Dr. Tyndall, during the past summer, in his ascent of Mont Blanc for the establishment of thermometric stations, I did not regard a few further experiments upon air from great altitudes as entirely superfluous; since the discovery of the causes determining the variations in the composition of the atmosphere will probably only be arrived at by the accumulation of vast numbers of observations made at various points at and above the earth's surface. It will also be perceived, on reference to the various analytical results above given, that, with the exception of M. Lewy, no experimenter has made contemporaneous determinations of the three chief gaseous constituents of the air; and I was therefore anxious, if possible, to render these samples available for the determination of carbonic acid, as well as of the two other chief gases.

The very minute changes of volume, which the instrument I use for gaseous analysis is capable of registering, led me to hope that it might not be impossible to make direct determinations of carbonic acid in the few cubic inches of air which are usually sealed up for analysis; and a number of estimations of the carbonic acid in air, collected at St. Bartholomew's Hospital, proved that this gas can be thus estimated, by absorption with caustic potash. Such an amount of air was taken for each determination, as was capable of supporting a column of mercury, from 600 to 800 millimeters high, which rendered any diminution of volume, to the extent of about $\frac{1}{7000}$ part, distinctly appreciable. The following results were obtained, those on the 26th of January, being seven successive determinations, extending over about three hours :

Date.	Percentage of Carbonic Acid.
Dec. 7, 1859	·042
Jan. 10, 1860	·064
„ „	·077
26, „	·098
„ „	·087
„ „	·098
„ „	·085
„ „	·098
„ „	·110
„ „	·101

Although it cannot be doubted that there are other methods by which carbonic acid can be more minutely and accurately determined, whenever they can be carried out with the usual conveniences of a laboratory at hand, yet it is very questionable, whether any of these processes can rival this purely eudiometrical one, in cases where the operations have to be performed in the midst of all the inconveniences attending an experimenter at great altitudes. Any such estimations, involving the weighing of potash tubes at intervals of several days, or even weeks, are obviously not worthy of implicit confidence. In the above mode of determination, the actual change of volume, self-corrected for temperature, aqueous vapour, &c., being actually observed by the operator, an error exceeding ·01 per cent., is probably rarely or never committed.

In the following analyses of air from Mont Blanc, the carbonic acid was absorbed by a single drop of concentrated solution of caustic potash, and the oxygen was then determined by exploding the residual gas with excess of electrolytically prepared hydrogen.

Specimen collected at the Grands Mulets (altitude 11,000 feet), August 20th, 1859, at 6·45 P.M. Wind, north, hail falling, but a moderately clear sky.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	539·5	5·0°
After absorption of carbonic acid .	538·9	5·0°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	290·8	5·2°
After admission of hydrogen . .	486·5	5·2°
After explosion	304·9	5·2°

III.

	Obs. vol.	Temperature C
Air used	248·7	5·2°
After admission of hydrogen . .	443·8	5·2°
After explosion	288·7	5·2°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	79·096	79·124	79·110
Oxygen .	..	20·793	20·765	20·779
Carbonic acid	0·111	..	..	·111
				100·000

Specimen taken at the summit (altitude 15,732 feet), August 21st, at 8·45 A.M. Wind, north; weather bright and sunny; air filled with particles of snow whirled up by the wind.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	326·1	5·2°
After absorption of carbonic acid .	325·9	5·2°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	166·8	5·3°
After admission with hydrogen .	273·0	5·3°
After explosion	168·1	5·3°

III.

	Obs. vol.	Temperature C.
Air used	159·9	5·3°
After admission of hydrogen . .	302·7	5·3°
After explosion	202·7	5·3°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	78·989	78·988	78·989
Oxygen .	..	20·950	20·951	20·950
Carbonic acid	0·061	..	..	·061
				100·000

Specimen collected at Chamonix (altitude 3000 feet), August 23rd, at 2 P.M. Wind north; sky clear.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	474·1	5·4°
After absorption of carbonic acid .	473·8	5·4°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	255·6	5·0°
After admission of hydrogen . .	455·8	5·0°
After explosion	295·5	5·0°

III.

	Obs. vol.	Temperature C.
Air used	217·4	5·0°
After admission of hydrogen . .	377·3	5·0°
After explosion	241·1	5·0°

Percentage of Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	79·045	79·067	79·056
Oxygen .	..	20·892	20·870	20·881
Carbonic acid	·063	..	..	·063
				100·000

So far as the nitrogen and oxygen are concerned, the composition of these samples of air falls within the limits of variation noticed by former experimenters; but, although the comparatively high percentage of carbonic acid, at the Grands Mulets, confirms the observations of the Messrs. Schlagintweit, as to the presence of a larger amount of this gas at great elevations, yet the diminution of the quantity to about the normal amount upon the summit, shows, either that this gas attains a maximum at a height of about 11,000 feet, and again diminishes above this altitude, or, as is much more probable, the percentage of carbonic acid is *generally, but not invariably,* greater in the higher regions of the atmosphere. These results also exhibit a correlation between atmospheric oxygen and carbonic acid, for when the one increases the other diminishes,—a fact which will be better seen from the following comparison:—

	Percentage of carbonic acid.	Mean percentage of oxygen, in air free from carbonic acid.
Grands Mulets . .	·111	20·802
Summit . . .	·061	20·963
Chamounix . . .	·063	20·894

This result, if it be confirmed, cannot be regarded as altogether unexpected, when we consider the effects of vegetation, combustion, and respiration upon the constituents of the atmosphere; but both this and the comparative amount of carbonic acid at great altitudes, are problems, the solution of which must be left to future and more extended inquiries.

VI.—*On Refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of Coinage.*

By Robert Warington.

Towards the latter end of the year 1857, I received from the Australian Bank, a specimen of bar-gold for analysis, which was stated to have been obtained from the quartz-crushing process. On the exterior, or what had been the surfaces of the original bar, it presented the general appearance of a golden hue, though perhaps, an experienced and critical eye, might have considered it a little paler than pure gold. Interiorly, or on the broken surface, however, it had a crystalline structure of a greyish yellow colour. It was very brittle and rotten, and by analysis, yielded the following results on the 100 parts.

Gold	92·50		
Silver	4·60		
Tin	2·00	with a trace of antimony	
Copper	0·75		
	99·75		
Loss	0·25		
			100·00

I have been informed that numerous bars of this white and brittle gold, had arrived in this country from Australia, and had caused much trouble and annoyance to the refiners, melters, and also to the Mint officers, as it will be evident, that the nature of the alloying metals is not rendered apparent in the ordinary mode of assay, by the processes of cupellation and quartation, they being oxidized, dissolved, and carried into the cupel with the lead; and that therefore, in the after larger operations of melting, when the gold passes forward for the purposes of coinage, the existence of the tin and antimony not having been discovered, is not provided for, and consequently, from the brittle nature of the alloy, the subsequent processes of rolling, to which it has to be subjected, are rendered impracticable. I am informed that about 47,000 ounces of gold bars have in this condition been returned to the Bank of England authorities from the Mint, as unfitted for the purposes of coinage.

A short time after the foregoing examination was completed and reported on, I received another specimen of this brittle gold for analysis, through other parties. This second sample presented somewhat the same appearances, both externally and internally, as the one just described, being perhaps, a little whiter in its colour, and more rotten or friable in texture. It yielded by analysis, on the 100 parts :—

Gold	93·80
Silver	2·20
Antimony	2·28
Tin	1·40
Arsenic Copper	traces
	99·68
Loss	0·32
	100

An interesting question arises from the above results as to the origin of these injurious alloying metals ; do they occur associated with the gold, or are they introduced during the melting process? As regards the first, we know that in stream works, gold and oxide of tin are commonly found associated, as is the case in Ceylon, in Cornwall, and other districts. We know also, that considerable quantities of stream-tin are brought from Australia. The presence, therefore, of that metal in small quantities, as an alloy, in the resulting gold bars, might be almost anticipated. But this view of the case does not account satisfactorily, for the other alloying metals found in the second analysis, particularly the antimony. My own impression, derived from a careful examination of the specimens and the foregoing results, is, that they are introduced during a rough process of refining, through the employment of sulphuret of antimony, and that, for want of efficient management, the operation has been imperfectly carried out.

The use of sulphuret of antimony, for the purpose of refining gold and raising its standard, is so well known, that I need hardly dilate upon it ; suffice it to say, that, if successfully applied, it converts the iron, zinc, tin, &c., that may be present, and much of the silver, into the form of sulphurets, which float, in their melted state, upon the surface of the gold ; a portion of the antimony at the same time alloying with that metal. This antimony should, of course, be afterwards removed by a second operation.* From a specimen which has since come into my possession, it will be seen that the particles of gold dust have been so imperfectly melted, before running into bars, that many of them are still visible in their flattened and rounded forms, and must therefore have remained suspended in the melted alloy. I feel that this explanation of the source of the alloying metals is, therefore, to some extent substantiated, as a want of a sufficiently high and continued heat would leave the gold very much in the state above described.

On delivering the report of this second analysis to the parties from whom I had received the sample, they were anxious to know if I could suggest to them a method by which these injurious alloys could be removed, and the gold rendered capable of being rolled or hammered, without, at the same time, greatly increasing the expense of the operations, or entailing a loss of the gold. I was in consequence induced to turn my attention to the effecting of this desirable object. The proper resolution of this problem required a little consideration, inasmuch, as, although it was evident that it must be accomplished by a process of oxidation, to burn out, as it were, the antimony and tin; yet it was also necessary that the oxygen should be applied to the alloyed gold while the metal was in its fluid state, and also that the oxidizing agent should not part with its oxygen simply by the high temperature to which it would be subjected.

Nitrate of potash I was informed had been suggested, tried and failed, although a very large percentage had been used; experiments in that direction were therefore considered unavailable, and my attention was consequently turned to the employment of metallic oxides having a weaker affinity for oxygen, at these high temperatures, than the metals which it was required to remove from the contaminated gold.

After a few experiments, all of which were more or less successful, I succeeded in obtaining the desired result, and submitted for the consideration of the parties concerned, a simple process, which, from their liberality, I was enabled at the time to communicate to several friends interested in such matters, and which I also desire now to lay before the members of the Chemical Society. The process consists in the employment of oxide of copper, about 10 per cent. of which is to be added to the alloyed gold, with the addition of a small quantity of borax, and the whole maintained in a well fused state for about half an hour. The result is a perfectly malleable gold containing a small percentage of metallic copper, and well fitted for the purposes of coinage. The proportion of oxide of copper used must of course greatly depend on the percentage quantity of the oxidable metal requiring to be removed; but I believe, from the specimens which I have worked on, that it never need exceed the 10 per cent. Oxide of manganese might be employed to effect the same purpose; but I found that the fusibility of the oxide of copper and its powerful fluxing properties, rendered its action much more efficient and complete, from its flowing continually over the surface of the molten gold, and thus thoroughly oxidizing and removing the tin and antimony from their combination. As thus conducted the resulting alloy should always be better than standard, unless the baser metals occur in very large proportion.

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* Since making this communication, I have been informed that sulphate of antimony also sometimes occurs in association with native gold in Australia.

By the action of nitro-hydrochloric acid upon these samples of alloyed gold, the resulting solution deposited on cooling beautiful crystals of chloride of silver; and I may be allowed here to mention a very curious case of the same kind, but to a much greater extent, which was brought under my notice some time since, by the late Mr. Maurice Scanlan. It appeared from his statement, that he had been requested to obtain the gold from a beautifully wrought and small sized rope-chain, of Indian manufacture; and on submitting it to the action of nitro-hydrochloric acid for this purpose, he found that it did not dissolve; and although he obtained some gold in solution, yet the form and size of the delicate fabric remained unaltered; it had become, however, very brittle and rotten, and was of a dingy brown colour. It was submitted to me for examination by the microscope, and when subjected to this scrutinizing agent, it was at once evident what had taken place, and of what the chain had been composed. It consisted almost entirely of chloride of silver, beautifully crystallised on the surface or strands of the rope, and having, in the cross section, a radiating structure from the interior to the circumference, the central core, in some fragments, exhibiting still a portion of the original alloy from which the gold had not been removed, it having, most probably, been protected from the action of the acid by the comparatively thick coating of chloride of silver which had been formed around it.

VI.—*On some Derivatives from the Olefines.*

By Frederick Guthrie.

II.

The terms *isotype* and *idiotype, isotypic* and *idiotypic* may be advantageously adopted to denote bodies which belong to similar types, or to the same one, and the relations which such bodies bear to one another. The application of these expressions, which are almost self-explicatory, is best seen in examples.

A body is idiotypic with all its replacement derivatives; the latter are, of course, idiotypic with one another; the whole are idiotypes.

Bodies belonging to the same chemical series are isotypic with one another or are isotypes. Hence

(1.) The idiotypes of the same body are idiotypes of one another.

(2.) The isotypes of the same body are isotypes of one another.

(3.) The idiotypes of the same body are isotypes of the idiotypes of an isotypic body.

(4.) The isotypes of the same body are isotypes of the idiotypes of an idiotypic or isotypic body.

In a paper read before the Chemical Society (March 3rd, 1859,) I described the formation and some of the properties of the bodies $C_4H_4Cl_2S_2$, $C_{10}H_{10}Cl_2S_2$, $C_{10}H_{10}ClS_2$ and of some derivatives obtained from them. I purpose now resuming the consideration of this interesting class of bodies obtained by the action of the two chlorides of sulphur upon the olefines, and rendering their history somewhat more complete, before discussing the behaviour of the other compound halogens towards the same hydrocarbons.

In the paper referred to, it was asserted that bisulphide of chlorine is without action upon ethylene at temperatures between 0° and 100° C. The hope was, however, expressed that the two might combine directly, as is the case with amylene, if they were subjected to increased pressure. I have since found that even at ordinary pressures, an increased temperature is sufficient to determine chemical recomposition; and from analogies, afterwards to be pointed out, I conclude that the most probable interpretation of such recomposition is the direct union of the two reagents, ethylene and bisulphide of chlorine, and the simultaneous decomposition of the product formed.

Action of bisulphide of chlorine upon ethylene.—Three or four ounces of bisulphide of chlorine are brought into a retort of two or three pounds capacity. The retort is connected with an inverted condenser, and through a tube, passing through the tubulus into the bisulphide, a rapid current of pure dry ethylene is allowed to pass. On heating the bisulphide to ebullition, the two substances are brought together in a gaseous state at a temperature of about 139° C.; a condition which appears greatly to promote their reaction. After about 200 litres of ethylene have passed through, the liquid which has deepened in colour, is transferred to a smaller retort and heated till the boiling point rises to 180° C. During this distillation, as well as during the passage of the ethylene, a disengagement of hydrochloric acid takes place. On allowing the residue in the retort to cool, a considerable quantity of sulphur separates out. The distillate, which contains only a small quantity of substance undecomposible by water, may be employed in subsequent operations. In order to free the organic compound in the unvolatilized residue from still adhering bisulphide of chlorine, it is, after separation from the sulphur, digested for many hours with water at 80°. After fresh portions of water no longer become acid, the residue, which is pasty and opaque, is allowed to stand for two or three days in contact with dilute caustic soda. After drying, it is digested with ether, and the same process of purification followed, which has been frequently described in my former paper.

In burning this substance with oxide of copper, it was weighed in an open boat and chlorate of potash was employed. This same method was used with the non-volatile bodies afterwards to be described. In the determination of the sulphur of this and other bodies, I have employed carbonate of zinc in conjunction with chlorate of potash, instead of the carbonates of soda or magnesia; the first of these attacks the glass, and the subsequent separation of silicic acid renders the filtration troublesome; the second is so light as to be prone to projection from the tube; and both are difficult to procure free from sulphuric acid. The carbonate of zinc prepared from the chloride, or the oxide of zinc prepared by the combustion of zinc, may, I think, in all cases advantageously replace the before-mentioned carbonates for sulphur determinations. The zinc may also be used in union with oxide of mercury in Russell's method. In all cases, however, the combustion tube should be about 20 inches long and the anterior eight inches should be kept cold.

I. 0·4637 grm. gave 0·3199 grm. carbonic acid and 0·0980 grm. water.

II. 0·2286 grm. gave 0·0445 grm. water.

III. 0·3960 grm. gave 0·2747 grm. carbonic acid and 0·0735 grm. water.

IV. 0·2564 grm. gave 0·4559 grm. sulphate of baryta.

V. 0·2876 grm. gave 0·6178 grm. chloride of silver.

Calculated.		Found.					
		I.	II.	III.	IV.	V.	Mean.
C_4 . .	18·45	18·81	„	18·92	„	„	18·86
H_3 . .	2·31	2·33	2·12	2·06	„	„	2·17
S_2 . .	24·61	„	„	„	24·35	„	24·35
Cl_2 . .	54·62	„	„	„	„	53·14	53·14
	99·99						98·52

The substance analysed has accordingly the composition $C_4H_3S_2Cl_2$ having been formed according to the equation—

$$C_4H_4 + 3S_2Cl = C_4H_3S_2Cl_2 + HCl + 4S$$

which also explains the liberation of hydrochloric acid and the separation of free sulphur, described in the preparation of the body. Probably the most appropriate name for this body would be the *bisulphochloride of chlorethylene,* its formula being

$$C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl$$

inasmuch as in all likelihood, one atom of hydrogen has been replaced by one of chlorine, and the so-formed chlorethylene has combined with the bisulphide of chlorine; or the bisulphide of chlorine has combined with the ethylene to $C_3H_4S_2Cl$, and this body has decomposed two more atoms of bisulphide of chlorine, forming hydrochloric acid and bisulphochloride of chlorethylene:

$$C_4H_4S_2Cl + 2S_2Cl = C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl + 4S + HCl$$

It is clear however that it may be viewed also, either as the bichlorosulphide of vinyl,

$$C_4H_3S_2Cl_2$$

which would however be without analogues, or as the bisulphide of bichlorethyl,

$$C_4 \begin{Bmatrix} H_3 \\ Cl_2 \end{Bmatrix} S_2.$$

Bisulphochloride of chlorethylene is a transparent liquid of light yellow colour. Its taste is sweet and pungent. Its smell when fresh is agreeable, being between those of peppermint and of oil of lemons. Three or four drops when swallowed produce headache. It is soluble in ether and alcohol, insoluble in water; it does not volatilize without decomposition. At 11° C. its specific gravity is 1·599.

It is worthy of note that the bichlorosulphide of ethylene $C_4H_4S_2Cl_2$ obtained by the direct union of chloride of sulphur with ethylene and described in the former paper, differs from the body just described only in having one more atom of hydrogen, a difference which might not appear on analysis. The specific gravity of the latter body however is only 1·408, its smell is quite distinct, and it is much less soluble in ether.

The determination of the composition of bisulphochloride of chlorethylene suggested three questions:—

(1.) Is its formation preceded by that of the bisulphochloride of ethylene $C_4H_4S_2Cl$, which undergoes decomposition on heating in presence of two additional molecules of S_2Cl?

(2.) May it be regarded as a substitution-product of bisulphide of ethyl, being in fact the bisulphide of bichlorethyl $C_4 \begin{Bmatrix} H_3 \\ Cl_2 \end{Bmatrix} S_2$?

(3.) Does it admit of further exchange of hydrogen for chlorine, whether such chlorine replacement-products be identical or not with the hitherto hypothetical chlorine substitution-products of bisuphide of ethyl.*?

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* Ann. Ch. Phys., [3], xviii. **Cahours** mentions that chlorine acts upon the bisulphide of ethyl; but the products do not appear to have been examined.

The question (1) may be answered approximately by submitting the bisulphochloride of amylene $C_{10}H_{10}S_2Cl$, described in the former paper to the action of two additional molecules of bisulphide of chlorine at a high temperature.

Question (2) must be answered by submitting bisulphide of ethyl to chlorine.

To answer question (3) bisulphochloride of chlorethylene must be acted on by chlorine.

On passing dry chlorine into bisulphochloride of chlorethylene, a rapid disengagement of hydrochloric acid results, accompanied by a liberation of heat which, under favourable circumstances, may raise the temperature of the liquid from 12° C. to 85° C.; at the same time the liquid loses almost all its colour. In the following experiments the reaction was carried on in the dark.

Through eight or ten grammes of bisulphochloride of chlorethylene, dry chlorine was passed, until the heat at first developed had abated, and the ordinary temperature was re-established. The tube containing the product was then heated in a water-bath to 100° C., and a rapid current of dry chlorine was passed through for two hours. The product was freed from dissolved hydrochloric acid and chlorine by being again heated to 100° C. and subjected to a rapid current of dry carbonic acid for two hours. Even after all the hydrochloric acid was expelled, the carbonic acid, in passing through the liquid at 100° C. continued to carry off a vapour which both fumed with ammonia and reddened litmus paper. This is due to the vapours of chloride of sulphur and oxychloride of sulphur as we shall presently see.

The cold gas-exit-tube became coated with a layer of yellowish transparent crystals, too small in quantity for examination, and consisting probably of oxychloride of sulphur, whose formation was due to a trace of moisture. After the carbonic acid had passed through during the time mentioned, a drop of the liquid did not give up any hydrochloric acid to water. It was, however, digested with warm water, dissolved in ether, then dried and purified as before.

On analysis this body showed the following composition:—

grm. grm. grm.
I. 0·3737 gave 0·2182 carbonic acid and 0·0374 water.
II. 0·5184 ,, 0·4116 sulphate of baryta.
III. 0·4453 ,, 1·2957 chloride of silver.

	Calculated.	Found.			
		I.	II.	III.	
C_4 . .	16·16	15·94	„	„	
H_2 . .	1·35	1·11	„	„	
S . .	10·76	„	10·88	„	
Cl_3 . .	71·73	„	„	71·98	
	100·00				99·91

The action of chlorine, therefore, under these circumstances upon the bisulphochloride of chlorethylen is to replace one atom of hydrogen by chlorine and to eliminate half the sulphur; thus giving rise to a body which may be called the *chlorosulphide of bichlorethylene.*

$$C_4\left\{\begin{matrix}H_2\\Cl_2\end{matrix}\right\}SCl.$$

The reaction takes place according to the equation

$$C_4H_3Cl_2S_2 \;+\; 3Cl \;=\; C_4H_2Cl_3S \;+\; HCl \;+\; 3Cl$$

The chlorosulphide of bichlorethylene is a yellowish, almost colourless, transparent liquid of pungent, suffocating, and most persistent smell. It mixes with ether and alcohol, but is insoluble in water. Although not volatile when heated alone, it may be volatilized almost without residue in a current of dry carbonic acid. Its specific gravity is 1·225 at 13·5° C.

In order to compare the products of the action of chlorine upon bisulphide of ethyl with those of its action upon the bisulphochloride of chlorethylene, ten or twelve grammes of the bisulphide of ethyl were exposed to the action of chlorine in the same apparatus, and as nearly as possible under the same physical conditions as obtained during the action of chlorine upon the bisulphochloride of chlorethylene.

On passing a rapid current of dry chlorine into the above quantity of bisulphide of ethyl, the temperature was raised from 14° to 78° C., abundance of hydrochloric acid being evolved. The first bubbles of chlorine, passed through the liquid, became opalescent, owing to the separation of sulphur. As, however, the temperature rose, this opalescence speedily disappeared. At one stage, the liquid became much darker in colour than the sulphide of ethyl; subsequently it regained its light straw-colour; when this happened, the evolution of heat ceased. The liquid product so formed was thereon heated to 100° C. in a water-bath, and the current of chlorine continued for two hours; it was then freed from hydrochloric acid and chlorine by a stream of carbonic acid, as described in the preparation of the chlorosulphide of bichlorethylene.

A product was thus obtained, having the same colour and precisely the same exceedingly characteristic smell as the chlorosulphide of bichlorethylene, formed, as already described, by the action of chlorine upon the bisulphochloride of chlorethylene. Its specific gravity was found to be 1·219 at 13·5° C., which is identical with that of the chlorosulphide of bichlorethylene.* Analysis also showed the two to contain the elements carbon, hydrogen, sulphur, and chlorine in the same proportions as they exist in the chlorosulphide of bichlorethylene.

I. 0·3623 grm. gave 0·2177 grm. carbonic acid and 0·0329 grm. water.

II. 0·4073 grm. gave 0·4113 grm. sulphate of baryta.

III. 0·2762 grm. gave 0·7702 grm. chloride of silver.

	Calculated.	Found. I.	II.	III.	
C_4	16·16	16·38	,,	,,	
H_2	1·35	1·00	,,	,,	
S	10·76	,,	11·10	,,	
Cl_3	71·73	,,	,,	69·00	
	100·00				97·48

This liquid has therefore the formula:—

$$C_4 \left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right\} S,$$

having been formed according to the equation:—

$$C_4H_5S_2 + 7Cl = C_4 \left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right\} S + SCl + 3HCl,$$

and being, in accordance with its derivation, the *sulphide of terchlorethyl.*

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* For exact comparison, the specific gravities of the two substances were taken in the same vessel and nearly at the same time.

I can detect no difference whatever between the substance just described, and that whose analysis was given on page 40, and named the chlorosulphide of bichlorethylene. The empirical formulæ of the two are identical, $C_4H_2Cl_3S$; but, if we insist upon evidencing the different sources of the two bodies in their formulæ and names, we must write the one:—

Chlorosulphide of bichlorethylene . $C_4\left\{\begin{matrix}H_2\\Cl_2\end{matrix}\right\}SCl$, the other

Sulphide of terchlorethyl . . . $C_4\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}S$.

That these two bodies are identical I believe no one who has had them in his hands will doubt. I must reserve the confirmatory evidence resulting from the apparent identity of some oxygen derivatives obtained in the same manner from both, for another occasion. But from the above facts alone we are perhaps justified in giving an affirmative answer to the question (2) above proposed; that is, we may look upon bisulphochloride of chlorethylene in its behaviour towards chlorine as a chlorine-substitution-product of bisulphide of ethyl. That we do not obtain the bisulphochloride of chlorethylene by acting upon bisulphide of ethyl with chlorine, is accounted for by the fact already proved, that the bisulphochloride of chlorethylene is itself attacked by chlorine. It is highly probable, however, that the darkening of the liquid, mentioned above, at one stage of the action of chlorine upon the bisulphide of ethyl, is owing to the formation of the bisulphochloride of chlorethylene, which subsequently undergoes further hydrogen-replacement and elimination of sulphur, being converted into the chlorosulphide of bichlorethylene. I did not, however, seek to intercept the process at this point, because no criterion could be formed of the integral nature of the action, and because even if a body of the anticipated composition had been formed, it might still have been a mixture of the higher substitution-product with the original substance.

The identity of the chlorine-substitution-products of $\left\{C_4\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl$ and $C_4H_5S_2$ is further of considerable interest, inasmuch as it shows that towards chlorine the two are essentially idiotypic, and that consequently, while we have seen, in the case of amylene, that a body, $C_nH_nS_2Cl$, acts towards oxides and hydrated oxides as the *chloride* of a *sulphur*-radicle; towards chlorine such a body acts as the *sulphide* of a *chlorine*-radicle. This line of evidence will be more complete after studying the action of chlorine upon the bisulphochloride of amylene previously described.

If a rapid current of dry chlorine be passed through bisulphochloride of amylene, $C_{10}H_{10}S_2Cl$, hydrochloric acid is evolved. In order to compare this reaction with the action of chlorine upon bisulphide of ethyl and bisulphochloride of chlorethylene, ten or twelve grammes of the bisulphochloride of amylene were brought into the same apparatus and subjected to the action of chlorine, under the same circumstances as attended the action of that element upon the bodies mentioned. The action was attended by an evolution of heat which raised the liquid from 12° to 70° C. The colour changed from a light straw-yellow to a garnet-red at this point I suppose the liquid to consist principally of an intermediate substitution-product $C_{10}\left\{\begin{matrix}H_9\\Cl\end{matrix}\right\}S_2Cl$), and then became almost of its original paleness. At this point no more heat was evolved. The product being then heated in a water-bath, the stream of chlorine was continued for two hours. After standing in a stoppered bottle for twelve hours, it still smelt strongly of chlorine. The excess of chlorine and the hydrochloric acid formed were finally expelled by a stream of dry carbonic-acid at 100° C., and the product was purified as before.

	Grm.		Grm.			Grm.	
I.	0·4853	gave	0·4334	carbonic acid	and	0·1572	water.
II.	0·3299	„	0·3228	„	„	0·1137	„
III.	0·4241	„	0·3850	„	„	0·1368	„
IV.	0·5011	„	1·2995	chloride of silver.			
V.	0·3940	„	0·2274	sulphate of baryta.			
VI.	0·6996	„	0·4031	„	„		
VII.	0·4942	„	0·2810	„	„		

Found.

	I.	II.	III.	IV.	V.	VI.	VII.	*mean.*
C	23·76	23·66	24·76	„	„	„	„	24·06
H	3·59	3·83	3·59	„	„	„	„	3·67
Cl	„	„	„	64·15	„	„	„	64·15
S	„	„	„	„	7·91	7·89	7·79	7·86
								99·74

The possible substance, whose composition approaches most nearly to this, is the *chlorosulphide of terchloramylene*,

$$C_{10}\left\{\begin{matrix}H_7\\Cl_3\end{matrix}\right\}SCl,$$

or, according to what has been shown concerning the ethylene compounds, the *sulphide of quadrochloramyl*,

$$C_{10}\left\{\begin{matrix}H_7\\Cl_4\end{matrix}\right\}S;$$

for these two bodies, to whose identity analogy points, require

C_{10} ..	26·66
H_7 ..	3·11
Cl_4 ..	63·11
S ..	7·11
	99·99

The sulphide of quadrochloramyl or chlorosulphide of terchloramylene closely resembles in smell, taste, and physical properties the ethylene substitution-products already discussed. It is a transparent, non-volatile, light yellow liquid of specific gravity 1·406 at 16° C. It is insoluble in water, miscible with ether, and soluble in hot alcohol.

Fourteen grammes of amylene were gradually mixed at the closed end of a combustion-tube, four feet long, with more than three equivalents of bisulphide of chlorine. The mixture, having been kept boiling for eight hours (during which hydrochloric acid was copiously evolved) was transferred to a retort and heated till its temperature rose to 190° C. After cooling and decanting from the small quantity of separated sulphur, the product was washed with aqueous caustic soda, etc.

0·4148 grm. gave 0·4411 grm. of carbonic acid and 0·1680 grm. water.

0·7006 grm. gave 0·6362 grm. of chloride of silver.

These numbers show 28·76 per cent. of carbon, 4·50 per cent. of hydrogen, and 22·46 per cent. of chlorine; a result which points to no simple formula. The product was probably a mixture.

It is very worthy of notice that the body resulting from the action of chlorine upon the bisulphochloride of amylene is not an analogue of that derived by chlorine from the bisulphochloride of chlorethylene (*i.e.* from the bisulphide of bichlorethyl) and from the bisulphide of ethyl. Comparing their general formulæ, we have for the first $C_{2n}\begin{Bmatrix}H_{2n-4}\\Cl_4\end{Bmatrix}S$, and for the second $C_{2m}\begin{Bmatrix}H_{2m-3}\\Cl_3\end{Bmatrix}S$.

But this difference, which might seem to indicate an anomalous behaviour in the two cases, really results from the symmetry of the two recompositions effected by chlorine; a symmetry which extends moreover, to the chlorine-substitution-products of the monosulphide of ethyl, studied by Regnault.[*] Putting the reations together:—

By the action of Chlorine.

	(1.)	(2.)	(3.)	(4.)
	C_4H_5S	$C_4H_5S_2$	$C_4\begin{Bmatrix}H_3\\Cl\end{Bmatrix}S_2Cl$	$C_{10}H_{10}S_2Cl$
is converted into	$C_4\begin{Bmatrix}H\\Cl_4\end{Bmatrix}S$	$C_4\begin{Bmatrix}H_2\\Cl_3\end{Bmatrix}S$	$C_4\begin{Bmatrix}H_2\\Cl_3\end{Bmatrix}S$	$C_{10}\begin{Bmatrix}H_7\\Cl_4\end{Bmatrix}S$
by the exchange of	4 H for 4 Cl	3 H for 3 Cl and SCl for Cl	H for Cl and SCl for Cl	3 H for 3 Cl Cl for SCl

Thus in all cases but the third, a fourfold exchange is effected; and that here, merely a twofold exchange occurs, may be attributed to the body, reckoned from the bisulphide of ethyl, having already suffered a two-fold replacement. It has been already shown in the first paper, that SCl is monomolecular, and may be replaced by a single atom of chlorine. Particularly remarkable is the analogy between (2) and (4), proving as it does, that these two substances are, *towards chlorine,* isotypic.

The above bodies, furnish examples of the proneness which chlorine has to replace even numbers of molecules.

In order to throw some more light upon the constitution of bisulphochloride of amylene, I have subjected that body to the action of nitric acid; but before describing the products obtained by this reaction, it will be well to consider briefly, the action of nitric acid upon amylene itself.

The temperature at which nitric acid and amylene act upon one another, is so far above the boiling point of the latter body, that great loss of amylene results if the two are heated together, even in capacious vessels, until the reaction commences. If five or six grammes of amylene be shaken in a bolt-head, with four or five times the volume of fuming nitric acid, and heat be applied until the acid boils, a sudden evolution of nitrogen-oxides results, the neck of the bolt-head becomes coated with a thin layer of fatty white crystals, and green oily drops, heavier than nitric acid, appear in that liquid. For the above-mentioned reason, however, this method of tracing the reaction was abandoned, and the following one employed.

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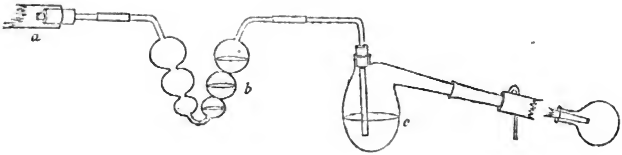
[*] Ann. Ch. Phys. [3], lxxi, 387.



Air, dried by passing over chloride of calcium, in the tube *a*, is made to bubble through amylene, contained in the bulbs *b*, and being thus charged with the vapour of amylene, it is led through fuming nitric acid in the retort *c*, which has previously been heated to boiling, and which is kept so during the passage of the gas. The retort is connected with a condenser. If the volume of the nitric acid be about seven times as great as that of the amylene, and if the current of air and the heat of the retort be so regulated, that the amylene and nitric acid are volatilized nearly together, almost the whole of the non-gaseous products consists of the white fatty crystalline substance before mentioned, which coats the surface of the receiver; the greater quantity, however, is deposited in the tube of the condenser, and may thence be washed into the receiver. Water is added to the latter, and it is vigorously shaken until the product cakes together.

Although heavier than water, it generally floats upon its surface, owing to the presence of small gas-bubbles. After washing with cold water on a funnel, and drying between blotting paper, it is strongly pressed to remove traces of the liquid product mentioned before, and then recrystallized from boiling anhydrous ether. If the ethereal solution be allowed to cool without evaporation, the substance crystallizes out in long rectangular prisms. If the crystallization be helped by evaporation, it separates as flat rectangular tables. Under the microscope, no other than right angles could be observed in either case.

Burnt with oxide of copper, metallic copper being employed in the anterior of the tube,

I. 0·3680 grm. gave 0·5019 grm. carbonic acid, and 0·2066 grm. water.

II. 0·1330 grm. gave 19·1 cc. of nitrogen at 0° C., and 760 mm.

	Calculated.	I.	II.
C_{10} . .	37·09	37·20	„
H_{10} . .	6·18	6·24	„
N_2 . .	17·28	„	18·04
O_8 . .			

This substance may, therefore, be called binitroxamylene, its formula being—

$$C_{10}H_8 2(NO_4)$$

A portion of the nitric acid is deoxidized to NO_2; this combines with the oxygen of the excess of air to form NO_4; and the latter molecule unites directly with a fresh portion of amylene. This same substance, which can be obtained only in small quantities by the above process, may be prepared in any desired quantity by the direct union NO_4 with amylene. The latter method of preparing this body, together with some of its properties, will appear in the next communication.

VII.—*On the Crystallised Hydrates of Baryta and Strontia*

By Charles L. Bloxam.

Considerable difference of opinion appears to exist among chemical authors with respect to the composition of the crystallised hydrates of baryta and strontia, some representing them as containing 8 eqs., others 9 eqs., and others even 10 eqs. of water, whilst in some cases these hydrates, so closely analogous in their chemical relations, are represented as crystallising with different amounts of water.

Having had occasion to satisfy myself with respect to their true composition, I beg to submit the results of my analysis to the Society.

The crystallised hydrate of baryta was prepared according to the method recommended by Mohr, by adding powdered nitrate of baryta to a boiling solution of an equivalent quantity of hydrate of soda. The crystals which separated from the cooled liquid were purified by two crystallisations.

On examining the solution from which the first crop of crystals had been deposited, it was found to contain a considerable quantity of undecomposed nitrate of baryta, together with some hydrate of soda, showing that the decomposition of the nitrate by a single equivalent of soda was far from complete. In a second preparation 1·4 eqs. of hydrate of soda were employed, but in this case also, a considerable quantity of the nitrate of baryta was left undecomposed, though less than in the first experiment.

The hydrate of baryta exhibited, in a remarkable degree, the tendency to remain, without crystallising, in a super-saturated solution, until it was either briskly stirred or placed in contact with a crystal of the hydrate.

On attempting to dry the crystals in vacuo over oil of vitriol, they soon became opaque, which was at first attributed to the formation of a thin film of carbonate, but was afterwards found to arise from loss of water; indeed the crystals were found to effloresce even in air of ordinary humidity, which may help to explain the discrepancy in the results which they have afforded to different analysts.

In order to determine the amount of water lost in vacuo over oil of vitriol, separate samples of the crystals, obtained in two distinct operations, were exposed in a receiver of air over quick lime, and weighed at short intervals, until the loss of weight in a given period suddenly diminished, and the first sign of efflorescence began to show itself upon the edges of the crystals.

Two determinations of adhering water made in this way gave respectively 1·39 and 1·24 per cent.

The dry crystals were then exposed in vacuo, over oil of vitriol, until they ceased to lose weight.

The effloresced hydrate thus obtained was heated to dull redness in a closely covered silver crucible, and weighed, at intervals of four or five minutes, until it began to increase in weight slightly, from absorption of carbonic acid.

The baryta was also precipitated and determined as sulphate, both in the original dry crystals and in the effloresced hydrate.

The subjoined table contains the results of these experiments, calculated for 100 parts of the dry crystallised hydrate.

	I	II	III	IV	V	VI	Mean.		Calculated (Ba = 68·5) BaO,HO + HO + 7Aq.	
Water lost in vacuo	39·36	39·30	39·69	39·84	39·63		39·56	45·59	40·00	45·71
" " on ignition	5·93	6·04	6·12				6·03		5·71	
Baryta				48·12	48·42	48·26	48·26			48·57

These numbers appear to warrant the conclusion that the formula of the crystallised hydrate of baryta is BaO,HO + 8Aq., and that of the effloresced hydrate BaO,HO + Aq, the pure hydrate BaO,HO being obtained by igniting the latter.

The effloresced hydrate suffered no more loss of water at 212° F, even in vacuo.

It is worthy of notice that this effloresced hydrate evolved much heat when moistened with water.

The crystallised hydrate of strontia was also prepared by decomposing the nitrate of strontia with hydrate of soda at the boiling point; in this case nearly 2 eqs. of the hydrate were employed for each equivalent of nitrate of strontia, and this salt was found to have been completely decomposed. The hydrate of strontia, however, did not dissolve in the liquid, like the hydrate of baryta, but separated in the form of a granular precipitate, which had the same composition as the crystallised hydrate. On pouring off the solution containing the nitrate of soda, and boiling this granular precipitate with successive portions of water, very large and beautiful crystals were obtained, which were purified by recrystallisation.

The crystals effloresced in the same way as those of hydrate of baryta. They were analysed in a similar manner, the strontia being completely precipitated by sulphuric acid and alcohol, and the sulphate of strontia subsequently washed with alcohol.

The results are seen in the following table.

	I	II	III	IV	Mean.		Calculated (Sr = 43·8) SrO,HO + HO + 7Aq.	
Water lost in vacuo . . .	47·79	47·75			47·77	60·40	47·44	61·00
" " on ignition . . .	12·61	12·65			12·63		13·56	
Strontia	39·12	39·04	39·12	39·06			39·00	

It appears then, as would be expected, that the formula of the crystallised hydrate of strontia is SrO,HO + 8Aq, and that of the effloresced hydrate SrO,HO + Aq, but that when this latter is heated to dull redness, it loses the whole of its water, anhydrous strontia being left.*

The effloresced hydrate did not lose any more water in the water-oven at 212° F, but when raised to this temperature in vacuo, it lost 12·89 per cent., or exactly one equivalent of water, thus becoming converted into the simple hydrate SrO,HO.†

Both this and the effloresced hydrate evolved heat when moistened with water.

The inferior power possessed by strontia to retain these two last equivalents of water, is another interesting example of the gradation constantly observed in the properties of baryta and strontia; and I must express my regret that want of leisure precludes me, for the present, from examining the crystallised hydrate of lime, which may be expected to occupy a still lower position with respect to its power of retaining water of crystallisation.

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* I find that this circumstance had been already pointed out by Denham Smith (Phil. Mag. [3], ix, 87), although chemical writers have still represented the hydrate of strontia as permanent at a red heat.

† The effloresced hydrate also lost nearly the whole of its second equivalent of water when exposed for a very long time over very concentrated oil of vitriol, in vacuo.

VIII.—*Miscellaneous Observations.*

By A. W. Hofmann.

II.

(Continued from Vol. X., p. 211.)

4. *Action of Nitrous Acid upon Nitrophenylene-diamine.*

The experiments of Gottlieb have shown that dinitrophenylamine, when boiled with sulphide of ammonium, is converted into a remarkable base crystallising in crimson needles, generally known as *Nitrazophenylamine*, and for which, in accordance with the views I entertain regarding its constitution, I now propose the name *Nitrophenylene-diamine.* I owe to the kindness of Dr. Vincent Hall a considerable quantity of this substance which is not quite easily procured. In preparing it, Dr. Hall has, in the first place, followed the succession of processes recommended by Gottlieb, viz., treatment of phenyl-citraconimide (citraconanile) with nitro-sulphuric acid, transformation of the nitro-substitute into dinitrophenylamine, and the reduction of the latter by sulphide of ammonium. In other experiments Dr. Hall has availed himself with the same advantage of phenyl-succinimide (succinanile), which, under the influence of a mixture of nitric and sulphuric acid, exhibits a deportment similar to that of the citraconyl-body. Dinitrophenyl-succinimide is readily transformed into dinitrophenylamine, which ultimately yields the crimson-coloured compound.

To the accurate description which Gottlieb has given of the preparation and the properties of this substance, I have scarcely to add a single word. The following remarks refer to an experiment made with the view of obtaining some insight into the molecular construction of the body. If, bearing in mind the numerous analogies of the radicals ethyl and phenyl, we assume that the latter by the loss of hydrogen may be converted into a diatomic molecule phenylene, C_6H_4,* corresponding to ethylene, the existence of a group of phenylene-bases corresponding to the ethylene-bases cannot be doubted.

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* H = 1, C = 12, O = 16, S = 32, etc.

Ethylamine $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$ Ethylene-diamine $\left.\begin{matrix}(C_2H_4)''\\H_2\\H_2\end{matrix}\right\}N_2$

Phenylamine $\left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N$ Phenylene-diamine $\left.\begin{matrix}(C_6H_4)''\\H_2\\H_2\end{matrix}\right\}N_2.$

The compound known as semibenzidam or azophenylamine, which Zinin obtained by exhausting the action of sulphide of ammonium on dinitrobenzol, agrees with the last-named body in composition. Those chemists, however, who have had an opportunity of becoming acquainted with the well-defined properties of ethylene-diamine, will not easily be persuaded to consider the uncouth dinitrobenzol-product, sometimes appearing in brown flakes, sometimes as a yellow resin rapidly turning green in contact with the air, as standing to phenylamine in a relation similar to that which obtains between ethylene-diamine and ethylamine. We much more readily admit a connection of this description between phenylamine and Gottlieb's crimson-coloured base, in which the clearly pronounced character of the former is still distinctly visible, although of necessity, modified by the further substitution which has taken place within the radical.

Phenylamine $\left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N$

Phenylene-diamine (?) $\left.\begin{matrix}(C_6H_4)''\\H_2\\H_2\end{matrix}\right\}N_2$

Nitrophenylene-diamine $\left.\begin{matrix}(C_6[H_3, NO_2])''\\H_2\\H_2\end{matrix}\right\}N_2.$

Does the latter formula really represent the molecular constitution of the crimson needles? The degree of substitution of this body might have been determined by the frequently adopted process of ethylation. But even a simpler and shorter method appeared to present itself in the beautiful mode of substituting nitrogen into the place of hydrogen, lately discovered by P. Griess. The red crystals undergo indeed with the greatest facility the transformation, which he has proved already for a great many derivatives of ammonia.

On passing a current of nitrous acid into a moderately concentrated solution of the nitrate of the base, the liquid becomes gently heated, and deposits, on cooling, a considerable quantity of brilliant white needles, the purification of which presents no difficulty; being sparingly soluble in cold, readily soluble in boiling water, the new compound requires only to be once or twice re-crystallised. Thus purified, the new substance forms long prismatic crystals frequently interlaced, white as long as they are in the solution, but assuming a slightly yellowish tint when dried, and especially when exposed to 100°; they are readily soluble both in alcohol and in ether. The new body exhibits a distinctly acid reaction; it dissolves on application of a gentle heat in potassa and ammonia, without, however neutralizing the alkaline character of these bases; it also dissolves in the alkaline carbonates, but without expelling their carbonic acid. The new acid fuses at 211° C., and sublimes at a somewhat higher temperature, with partial decomposition. The sublimate consists of small prismatic crystals. Analysis gave the following results:—

I. 0·3290 grm. acid dried at 100°, gave
0·5298 „ carbonic acid, and
0·0777 „ water.

II. 0·2868 grm. acid gave 84 cc. moist nitrogen at 15°, and 0·7583 Bar. (corr.)

These numbers lead to the ratio:—

$$C_3H_2N_2O,$$

and, the origin of the substance being taken into consideration, to the formula:—

$$C_6H_4N_4O_2.$$

	Theory.		Experiment.	
			I.	II.
C_6	72	43·90	43·92	—
H_4	4	2·44	2·62	—
N_4	56	34·15	—	34·32
O_2	32	19·51	—	—
	164	100·00		

This formula is confirmed by the analysis of the silver- and of the potassium-compound.

Silver-salt. This salt is obtained in the form of a white amorphous precipitate on mixing the saturated ammonia-solution of the acid with nitrate of silver. *In vacuo* this salt may be dried without decomposition; at 100° it becomes slightly coloured; when gently heated on platinum foil it detonates. The silver therefore had to be estimated as chloride.

I.	0·4215	grm.	silver-salt gave
	0·4068	,,	carbonic acid, and
	0·0487	,,	water.
II.	0·2984	,,	silver-salt gave
	0·1574	,,	chloride of silver.

The formula $C_6[H_3Ag]\,N_4O_2$ involves the following values :—

		Theory.	Experiment.	
			I.	II.
C_6	72	26·57	26·32	—
H_3	3	1·11	1·28	—
Ag	108	39·85	—	39·67
N_4	56	20·66	—	—
O_2	32	11·81	—	—
	271	100·00		

Potassium-salt. Obtained in pretty well-formed, flattened prisms, by saturating a moderately concentrated boiling solution of potassa with the acid; the crystals are difficultly soluble in potassa, but exceedingly soluble in pure water and in alcohol; the recrystallization is therefore attended with very considerable loss. The aqueous solution of the salt yields a crystalline precipitate on addition of potassa. The salt, even after four or five recrystallizations from alcohol, retains a distinctly alkaline reaction. Its composition was fixed by a potassium determination.

0·2012	grm.	salt dried at 100° gave
0·0857	,,	sulphate of potassium.

The formula $C_6\,[H_3K]\,N_4O_2$ requires the following values:—

	Theory.		Experiment.
C_6	72	35·64	—
H_3	3	1·48	—
K	39	19·31	19·10
N_4	56	27·72	—
O_2	32	15·85	—
	202	100·00	

With regard to the other salts, I have made but few observations.

The ammonium-salt crystallizes in needles. It has, however, but little stability, losing the whole of the ammonia when repeatedly recrystallized. The solution of this salt exhibits with metallic oxides the following deportment.

Barium and calcium-salts are not precipitated. Salts of copper give a light blue, salts of nickel a light green precipitate. The solution of a ferrous salt produces a deep brown-red precipitate, probably with simultaneous decomposition of the acid; the solution of a ferric salt, a light fawn-coloured precipitate. The salts of lead, zinc, manganese, and mercury (*mercurosum* and *mercuricum*), furnish white flaky precipitates.

The analysis of the new compound shows that, under the influence of nitrous acid on nitrophenylene-diamine, one molecule of nitrogen is substituted into the place of three molecules of hydrogen, which are eliminated in the form of water

$$\underbrace{C_6H_7N_3O_2}_{\text{Nitrophenylene-diamine.}} + HNO_2 = 2\,H_2O + \underbrace{C_6[H_4N]N_3O_2}_{\text{New acid.}}$$

I do not propose a name for the new compound, which can claim but a passing interest, as throwing by its formation some light on the constitution of nitrophenylene-diamine.

The composition of the new acid and of its salts shows that in the crimson base four hydrogen molecules are still capable of replacement; in other words, that this body still contains four extra-radical molecules of hydrogen. These experiments appear to confirm the view which in the commencement of this note, I have taken of the constitution of the body; at all events, the mutual relation of the several compounds is satisfactorily illustrated by the formulæ—

Nitrophenylene-diamine $\left.\begin{array}{r}(C_6[H_3NO_2])'' \\ H_2 \\ H_2\end{array}\right\}N_2$

New acid $\left.\begin{array}{r}(C_6[H_3NO_2])'' \\ N''' \\ H\end{array}\right\}N_2$

Silver-salt $\left.\begin{array}{r}(C_6[H_3NO_2])'' \\ N''' \\ Ag\end{array}\right\}N_2.$

If the admissibility of this interpretation be confirmed by further experiments, the reaction discovered by Griess furnishes a new and valuable method of recognising the degree of substitution in the derivatives of ammonia.

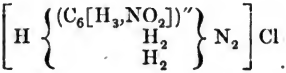
The new acid differs in many respects from the substances similarly produced from other nitrogenous compounds. As a class, these substances are remarkable for the facility with which they are changed under the influence of acids and more especially of bases. The new acid exhibits remarkable stability; it may be boiled either with potassa or with hydrochloric acid without undergoing the slightest change. Even a current of nitrous acid passed into either the aqueous or alcoholic solution is without the slightest effect. The latter experiment was repeatedly performed; for if the action of nitrous acid in a second phase of the process had assumed the form so frequently observed by Piria and others, it might have led to the formation of the diatomic nitrophenylene-alcohol, according to the equation

$$\left.\begin{array}{r}(C_6[H_3,NO_2])'' \\ H_2 \\ H_2\end{array}\right\}N_2 + 2HNO_2 = 2H_2O + N_4 + \left.\begin{array}{r}(C_6[H_3,NO_2])'' \\ \\ H_2\end{array}\right\}O_2.$$

It deserves to be noticed that nitrophenylene-diamine, although derived from two molecules of ammonia, is, nevertheless, a decidedly mono-acid base. Gottlieb's analyses of the chloride, nitrate, and sulphate, left scarcely a doubt on this point. However, as some of the natural bases, quinine, for instance, are capable of combining either with one or with two molecules of acid, I thought it of sufficient interest to confirm **Gottlieb's** observations by some additional experiments. The crystals deposited on cooling from a solution of nitrophenylene-diamine in concentrated hydrochloric acid were washed with the same liquid, and dried *in vacuo* over lime.

0·3975 grm. substance gave
0·3005 „ chloride of silver = 18·70 p. c. of chlorine.

The formula



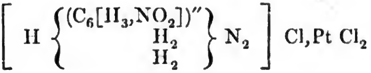
$$\left[H\left\{\begin{matrix}(C_6[H_3,NO_2])'' \\ H_2 \\ H_2\end{matrix}\right\}N_2\right]Cl$$

requires 18·73 p. c. of chlorine.

The dilute solution of the previous salt is not precipitated by dichloride of platinum; nor could the double salt of the two chlorides be obtained by evaporating the mixture of the two solutions, which, just as **Gottlieb** observed, was readily decomposed with separation of metallic platinum. I had, however, no difficulty in preparing a platinum-salt, crystallizing in splendid long brown-red prisms, by adding the platinum solution to the concentrated solution of the hydrochlorate.

0·4225 grm. of the platinum-salt dried *in vacuo*, left on ignition 0·115 grm. = 27·22 p. c. of platinum.

The theoretical percentage of the formula



$$\left[H\left\{\begin{matrix}(C_6[H_3,NO_2])'' \\ H_2 \\ H_2\end{matrix}\right\}N_2\right]Cl,Pt\,Cl_2$$

is 27·48 p. c. of platinum.

These experiments prove that, even under the most favourable circumstances, nitrophenylene-diamine combines with only 1 eq. of acid, while the ethylene-derivatives are decidedly diacid. The diminution of saturating power in nitrophenylene-diamine at the first glance seems somewhat anomalous; but the anomaly disappears if the constitution of the body be more accurately examined. It cannot be doubted that the diminution of the saturating power is due to the substitution which has taken place within the radical of the diamine. I pointed out some time ago,* that the basic character of phenylamine itself is considerably modified by successive changes induced in the phenyl-radical by substitution. Chlorphenylamine, though less basic than the normal compound, still forms well-defined salts with the acids; the salts of dichlorphenylamine, on the other hand, are so feeble, that under the influence of boiling water they are split into their constituents; and in trichlorphenylamine the basic character has entirely disappeared. Again, on examining the nitro-substitutes of phenylamine, we find that even nitrophenylamine is an exceedingly weak base, whilst dinitrophenylamine is perfectly indifferent. What wonder, then, that a molecular system, to which, in the normal condition, we attribute a diacid character, should, by the insertion of special radicals, be reduced to monoacidity? The normal phenylene-diamine, which remains to be discovered, will, doubtless, be found to be diacid, like the diamines derived from ethylene. Even now the group of diacid diamines is represented in the naphtyl-series.

$$\text{Naphtylamine} \qquad \left.\begin{matrix} C_{10}H_7 \\ H \\ H \end{matrix}\right\} N\text{, monoacid.}$$

$$\text{Naphtylene-diamine} \qquad \left.\begin{matrix} (C_{10}H_6) \\ H_2 \\ H_2 \end{matrix}\right\} N_2\text{, diacid.}$$

The body which I designate by the term naphtylene-diamine is the base which Zinin obtained by the final action of sulphide of ammonium upon dinitronaphtalin. This substance, originally designated as seminaphtalidam, and subsequently described as naphtalidine, combines, according to Zinin's experiments, with two equivalents of hydrochloric acid.†

I must add a remark suggested by the perusal of an interesting paper lately published by Kolbe.‡ In this paper, Kolbe refers to an outline of the history of ammonia and its derivatives, which, in the form of an evening lecture, I gave to the members of this Society, and which was subsequently printed in this journal.§ Kolbe regards many of the ammonia-compounds from a different point of view and expresses them by molecular formulæ different from those which I have adopted. It is not my intention to refer in detail to the several questions which he discusses, more especially since many of the theoretical views in which we differ were brought forward by others, and were simply introduced into the sketch with the view of rendering it as complete as possible; yet I must not allow this opportunity to pass without a word or two in elucidation of a question on which we differ more in appearance than in reality.

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* Mem. of Chem. Soc., ii, 298.

† Ann. Ch. Pharm. lxxxv, 328.

‡ Ueber den natürlichen Zusammenhang der organischen mit den unorganischen Verbindungen.—Ann. Ch. Pharm. cxiii, 293.

§ Chem. Soc. Qu. J. xi, 252.

In classifying the basic ammonia-derivatives, I proposed to designate the substances formed by the coalescence of more than one molecule of ammonia, in accordance with the nomenclature adopted for the neutral derivatives, and to distinguish, as monamines, diamines, and triamines, the bases derived from one, two, or three molecules of ammonia. In a classification of this kind the circumstance could not be left unnoticed, that many of the diamines and triamines combine with one equivalent of acid only, instead of saturating, as might have been expected from their construction, two or three equivalents. I was thus naturally led to subdivide again, and to distinguish, for instance, monoacid and diacid diamines, and I added: "It is obvious that the question, whether a diamine is capable of uniting with one or two equivalents of acid, must be intimately connected with the molecular construction of the basic system. As yet the nature of this connection remains unknown."

In the paper quoted, Kolbe remarks: "There appears no reason why, among the bodies derived from two molecules of ammonia, there should be, side by side with the diatomic substances, others yielding monoatomic ammonium-compounds. I cannot, therefore, consent to regard the ureas, melaniline, and other bases containing two atoms of nitrogen, as true diamines."

It is scarcely necessary to state that I entirely agree with my friend if he views as true diamines those bases which unite with two equivalents of acid; for it is proved experimentally, that the ureas and melaniline combine with one equivalent of acid only. All depends upon the definition of the word diamine. I had designated by this name basic compounds derived from two molecules of ammonia, without reference to the degree of saturating power; and even now it appears to me somewhat arbitrary to limit this term to those substances which unite with two equivalents of acid, especially since there are diatomic bases which are capable of combining either with one or with two equivalents of acid.

5. *Action of Bisulphide of Carbon upon Amylamine.*

In a note on the alleged transformation of thialdine into leucine, communicated some time ago* to the Chemical Society, I alluded to a crystalline substance observed by Wagner, when he submitted amylamine to the action of bisulphide of carbon. Wagner had not analysed this substance, but, considering its mode of formation, he had suggested that it might possibly be thialdine:

$$\underbrace{C_5H_{13}N}_{\text{Amylamine.}} + CS_2 = \underbrace{C_6H_{13}NS_2}_{\text{Thialdine.}}\dagger$$

A simple comparison of the properties of thialdine with those of the substance produced by the action of bisulphide of carbon upon amylamine, had enabled me at once to recognise the difference between the two bodies; and, satisfied with the result, I had not at the time examined more minutely into the nature of the latter substance.

The new interest conferred by recent researches upon leucine and its homologues, has recalled my attention to the sulphuretted derivative of amylamine.

This body may be readily procured by mixing anhydrous amylamine with a solution of dry bisulphide of carbon in anhydrous ether. The mixture becomes warm, and deposits, on cooling, white shining scales, which are insoluble in ether, and may therefore be purified by washing them with this liquid. The new body is likewise insoluble in water, but readily dissolves in alcohol; when dry, it may be exposed for a while to a temperature of 100° C. without fusing; after some time, however, the substance begins to be liquefied and to undergo complete decomposition, sulphuretted hydrogen being evolved. The same change occurs, although more slowly, at the common temperature; a mixture of free sulphur with a new crystalline body, extremely fusible, insoluble in water, but soluble both in alcohol and ether, remaining behind.

I. 0·274 grm. of the amylamine-body burnt with a mixture of oxide of copper and chromate of lead, gave 0·535 grm. of carbonic acid, and 0·2535 grm. of water.

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* Chem. Soc. Qu. J. x, 193.

† $H=1, C=12, O=16, S=32$.

II. 0·429 grm. of substance, dissolved in alcohol and boiled for some time with nitrate of silver, gave 0·837 grm. of sulphide of silver.

These numbers lead to the formula

$$C_{11}H_{26}N_2S_2 = C_6H_{13}NS_2, C_5H_{13}N.$$

	Theory.		Experiment. I.	Experiment. II.
C_{11}	132	52·8	53·25	—
H_{26}	26	10·4	10·28	—
N_2	28	11·2	—	—
S_2	64	25·6	—	25·17
	250	100·0		

The new substance then is formed simply by the union of two molecules of amylamine with one molecule of bisulphide of carbon.

$$\underbrace{2C_5H_{13}N}_{\text{Amylamine.}} + CS_2 = \underbrace{C_{11}H_{26}N_2S_2}_{\text{New compound.}}$$

A glance at this formula suffices to characterize this substance as amyl-sulphocarbamate of amylammonium.

$$C_{11}H_{26}N_2S_2 = \left.\begin{matrix}[(CS)''\ (C_5H_{11})\ HN] \\ [(C_5H_{11})\ H_3N]\end{matrix}\right\} S.$$

This view is readily confirmed by experiment. Addition of hydrochloric acid to the crystalline compound immediately separates an oily liquid which gradually solidifies, and the acid solution then contains amylamine which may be liberated by potassa. The oily substance is obviously amyl-sulphocarbamic acid. This body is readily soluble in ether, by which it may be separated from the chloride of amylammonium; it dissolves in ammonia and in potassa; mixed with amylamine it reproduces the original crystalline compound.

Experiments with ethylamine have furnished perfectly analogous results. I have been satisfied to establish qualitatively the analogy of the reactions.

It is of some interest to compare the deportment of amylamine under the influence of bisulphide of carbon with that of phenylamine in the same conditions. If these two bodies gave rise to similar changes, we should expect, in the case of phenylamine, the formation of phenyl-sulphocarbamate of phenylammonium. But experiment proves that phenylamine produces diphenyl-sulphocarbonyl-diamide (sulphocarbanilide), sulphuretted hydrogen being evolved :—

$$\underset{\text{Phenylamine.}}{\underline{2C_6H_7N}} + CS_2 = \underset{\text{Diphenyl-sulpho-carbonyl-diamide.}}{\underline{C_{13}H_{12}N_2S}} + H_2S.$$

Nevertheless it is extremely probable that further experiments will establish the perfect analogy in the deportment of amylamine and phenylamine with bisulphide of carbon. Diphenyl-sulphocarbonyl-diamide is probably the product of decomposition of a very unstable phenyl-sulphocarbamate of phenylammonium—

$$\underset{\text{Phenyl-sulphocarbamate of phenylammonium.}}{\underline{C_{13}H_{14}N_2S_2}} = H_2S + \underset{\text{Diphenyl-sulphocarbonyl-diamide.}}{\underline{C_{13}H_{12}N_2S,}}$$

while a more minute examination of the crystalline substance obtained by the action of heat upon amyl-sulphocarbamate of amylammonium cannot fail to characterize it as diamyl-sulphocarbonyl-diamide.

$$\underset{\text{Amyl-sulphocarbamate of amylammonium.}}{\underline{C_{11}H_{26}N_2S_2}} = H_2S + \underset{\text{Diamyl-sulphocarbonyl-diamide.}}{\underline{C_{11}H_{24}N_2S}}$$

The apparent dissimilarity of the two reactions would thus be reduced to the unequal stability of the sulphocarbamic acids of the amyl- and phenyl-series.

6. *On the use of Pentachloride of Antimony in the Preparation of Chlorine-compounds.*

Under a cloudless sky nobody would think of preparing the tetrachloride of carbon by any other process than by acting with chlorine upon chloroform. Exposed to direct sunlight, chloroform, when distilled in an atmosphere of chlorine, is rapidly converted into tetrachloride of carbon. A London November sky is, however, rather unfavourable to this process, and when requiring lately, for some experiments, a small quantity of the tetrachloride, I was compelled to have recourse to another method. A well-known process, for which we are indebted to Prof. Kolbe, consists in submitting the bisulphide of carbon to the action of chlorine at a red heat, when chloride of sulphur and chloride of carbon are formed. I have repeatedly availed myself of this process, which, when a large quantity of chloride of carbon is to be prepared, leaves nothing to be desired. When, however, a small amount is rapidly required, the apparatus involved in this process becomes rather inconveniently troublesome.

I have, therefore, endeavoured to substitute chlorine in a state of combination for the free chlorine. Pentachloride of phosphorus, as is well known, exerts so little action upon bisulphide of carbon, that it has been found convenient to prepare the pentachloride of phosphorus by saturating a solution of phosphorus in bisulphide of carbon with chlorine gas. There is likewise, no reaction between pentachloride of phosphorus and bisulphide of carbon at 100° under pressure; it is only at a higher temperature that an action takes place. A very different result is obtained when the latter compound is submitted to the action of pentachloride of antimony, the chlorinating properties of which were first noticed by Wöhler.

On adding pentachloride of antimony to bisulphide of carbon, a transparent mixture is obtained, which exhibits, after a few minutes, a powerful reaction, becoming very hot, and assuming a dark reddish-brown colour; the mixture deposits on cooling a copious crystallization of terchloride of antimony, interspersed with well-formed sulphur-crystals. The liquid poured off from the crystals consists chiefly of tetrachloride of carbon, retaining some bisulphide of carbon, chloride of sulphur, and terchloride of antimony:—

$$CS_2 + 2SbCl_5 = CCl_4 + 2SbCl_3 + S_2.$$

I had expected that the reaction would give rise to the formation of a compound $SbCl_3S$; but I have always found that the terchloride of antimony and the sulphur are separately deposited; and the same observation was made by Mr. H. McLeod, who has frequently carried out this reaction in my laboratory, modifying the proportions and the conditions of the experiment to a considerable extent. The small quantity of chloride of sulphur, which is simultaneously formed, appears to be the product of a secondary reaction, a portion of the pentachloride not yet acted upon being reduced by the separated sulphur.

If the experiment be made with a couple of ounces, the two liquids must be mixed in a flask provided with a vertical cooling apparatus; the reaction is so powerful, that a considerable quantity of the material would be lost without this precaution. Whilst studying this process, I have allowed the two liquids to act upon each other in various proportions: on employing 1 eq. of bisulphide of carbon (1 part by weight) and 2 eq. of pentachloride of antimony (8 parts by weight) the decomposition is pretty complete; on account of the formation of chloride of sulphur, however, the theoretical quantity of chloride of carbon is never reached. The process yields a much more copious result when the pentachloride of antimony is mixed with a considerable excess of bisulphide of carbon, and the mixture, whilst boiling in a retort, is submitted to the action of a current of chlorine gas. In this manner large quantities of bisulphide of carbon may be transformed into the tetrachloride by the intervention of a comparatively small quantity of pentachloride of antimony.

In order to purify the tetrachloride of carbon, the product of the reaction is submitted to distillation; the liquid passing over below 100° is boiled for some time with a solution of potassa, which removes terchloride of antimony and chloride of sulphur, together with any undecomposed bisulphide of carbon. From the product, boiling at a higher temperature, a considerable quantity of pure terchloride of antimony may be recovered.

The tetrachloride obtained by this process exhibits all the properties of the product obtained by other modes of preparation. It boils at 77°. The determination of the chlorine gave the following results:—

0·195 grm. of substance, ignited with lime, furnished 0·730 chloride of silver.

	Theory.		Experiment.
C	12	7·79	—
Cl_4	142	92·21	92·56.
	154	100·00	

Pentachloride of antimony may be used with advantage in many cases as a carrier of free chlorine. On heating a very moderate quantity of pentachloride of antimony in a retort connected with an inverted cooling apparatus, and passing simultaneously currents of dry olefiant gas and chlorine through the boiling liquid, a very large amount of Dutch liquid may be obtained in an exceedingly short time. In an atmosphere of pentachloride of antimony, the combination of the ethylene and the chlorine goes on with the greatest facility. As soon as the retort is filled with the Dutch liquid, the access of the two gases is interrupted, and the liquid distilled. The portion boiling below 100° requires only to be once more rectified in order to furnish perfectly pure bichloride of ethylene. The residue in the retort consists of a mixture of terchloride and pentachloride of antimony, which may serve for a new experiment.

The preparation of large quantities of pentachloride of antimony presents no difficulty whatever, since antimony combines readily with chlorine at the common temperature. A simple mode of proceeding consists in introducing the antimony, coarsely powdered, into a combustion-tube from 5 to 6 feet long, rising at an angle of 10° or 15°, one end of which is fitted into one tubulature of a two-necked glass globe, the other neck of the globe communicating with a tube supplying dry chlorine gas. The combination taking place in the tube, the product flows backwards into the globe, whilst the long layer of antimony prevents the escape of any chlorine.

7. *On Di-iodide of Methylene.*

Being engaged in some experiments on the action of chloride of carbon CCl_4 on the phosphorus-bases, I thought it desirable to study likewise the deportment of these substances under the influence of the corresponding iodide. Bearing in mind the facility with which chloroform is converted into chloride of carbon, I had some hope of procuring the iodide by the action of dry iodine upon iodoform:—

$$CHI_3 + I_2 = HI + CI_4 \text{ (?)}$$

When a mixture of iodoform and iodine, in the equivalent proportions of the above equation, was exposed in sealed tubes to a temperature of from 140° to 150°C., the iodoform was found to be changed after the lapse of some hours. On opening the tubes, an acid gas was evolved; and on distilling the dark solid residue with water, an aromatic body passed over, which collected in the receiver in the form of heavy oily drops. Decolorized by potassa and freed from water by chloride of calcium, the oily body boiled at about 180°, a considerable portion being decomposed, with evolution of hydriodic acid, and the distillate reassuming the red coloration. The liquid was therefore distilled *in vacuo;* it then passed over colourless, and without decomposition, at a temperature scarcely higher than the boiling point of water.

I. 1·222 grm. of substance, burnt with chromate of lead, gave 0·2077 grm. of carbonic acid, and 0·0800 grm. of water.

II. 0·705 grm. of substance burnt with lime, furnished 1·243 grm. of iodide of silver.

These numbers represent the composition of di-iodide of methylene—

$$CH_2I_2$$

only recently discovered by Boutlerow.*

Theory.			Experiment.	
			I.	II.
C	12	4·48	4·63	—
H_2	2	0·74	0·73	—
I_2	254	94·78	—	95·27
	268	100·00		

The compound analysed was indeed pure di-iodide of methylene. At a temperature near the freezing point of water, it solidified in large crystalline plates, and exhibited in every respect the properties described by Boutlerow. The analysis of the substance received moreover additional confirmation in a variety of substitutions in which it was subsequently employed.

The idea naturally suggested itself that the free iodine had no share in the formation of the di-iodide of methylene in the process described, but that the transformation of the iodoform was exclusively due to the action of heat. Experiment has verified this anticipation. Iodoform, when heated by itself in sealed tubes, at a temperature of 150°C. for several hours, furnished, on subsequent distillation with water, a very appreciable quantity of di-iodide of methylene. A comparative experiment, in which I followed the plan recommended by Boutlerow (1 eq. of iodoform, and 3 eqs. of ethylate of sodium), leads me to think that the action of heat yields a larger product and involves on the whole a far less troublesome operation. The inequality of the amount of product in my experiments, however, may possibly be ascribed to the circumstance that I have repeatedly prepared the methylene-compound by exposing iodoform to the action of heat alone, while Boutlerow's process was only once or twice adopted.

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* Compt. rend. xlvi, 595.

The transformation of iodoform into di-iodide of methlene by one or other of these processes is strange enough, and as yet remains entirely unexplained; there is formed, together with the methylene-compound, a quantity of a brown substance, the nature of which appears anything but attractive.

8. *Dibromide of Ethylene.*

The usual mode of preparing this compound, which of late has acquired considerable interest, consists in passing ethylene into bromine covered with a layer of water. This method is extremely tedious, since, in order to avoid the loss of both bromine and of ethylene, the gas can be but slowly transmitted through the liquid. The compound may, however, be rapidly obtained without the slightest loss, by an exceedingly simple modification of the process.

A strong glass bottle, of 2 or 3 litres capacity, is provided with a perforated cork, through which is fitted a glass tube open at both ends, one of which reaches nearly to the bottom of the bottle, whilst the other, slightly projecting over the cork, communicates by means of a flexible india rubber tube with the gasholder containing the ethylene. To start the operation, the bottle is detached, and filled over water with ethylene gas, into which are then poured from 100 to 130 grm. of commercial bromine, and about half that quantity of water, the cork with the glass tube being immediately replaced. On gently agitating the bottle, the ethylene is rapidly absorbed, and on turning the stop-cock of the gasholder, the gas rushes into the bottle exactly as into a vacuum. If the agitation be continued, a very large volume of ethylene may be thus united with bromine in an exceedingly short space of time, without the loss of a particle of the constituents or of the compound. As soon as the absorption becomes languid, the bromine is renewed, and the process continued in this manner until the accumulation of the dibromide renders it desirable to interrupt the operation. When working upon a very large scale, it is convenient to insert between the absorption-bottle and the gasholder a wash-bottle filled with water or dilute potassa, which serves as a gauge for the rapidity of the gas-current, purifying the gas at the same time, if necessary, and intercepting, moreover, any bromine-vapour that may have risen into the india rubber tube, if the mixture should have become hot, in consequence of too rapid absorption.

9. *Metamorphosis of Monobrominated Ethylene.*

A quantity of monobrominated ethylene (bromide of vinyl) was sealed up in a glass tube with the view of preserving it. After the lapse of a night, the colourless extremely mobile liquid was found to have become a white porcelain-like mass, and on opening the tube all pressure had disappeared. The white substance was perfectly amorphous and inodorous, and proved insoluble in water, in alcohol, and in ether. When heated it was charred, with abundant evolution of hydrobromic acid.

Analysis showed, as might have been expected, that the alteration of the monobrominated ethylene had been simply molecular.

0·2954 grm. substance, burnt with chromate of lead, gave 0·24784 grm. of carbonic acid and 0·0780 grm. of water.

The values corresponding to the formula C_2H_3Br are:—

	Theory.		Experiment.
C_2	24	22·43	22·87
H_3	3	2·80	2·93
Br	80	74·77	—
	107	100·00	

The chemical relations of bromide of vinyl are as yet but slightly examined. From its formula, the body might be considered as the hydrobromic ether of an alcohol homologous to allylic alcohol; this mode of viewing it, however, is not supported by the general deportment of the compound. The peculiar molecular transformation which it undergoes points rather to aldehydic relations, aldehyde being isomeric with the alcohol in question. As in the case of aldehyde, the conditions involving these transformations are utterly unknown; I have vainly tried to fix the circumstances under which the solid modification of bromide of vinyl is formed. In some cases the liquid bromide was preserved for weeks without the slightest change, when suddenly the liquid was found to have been transformed throughout its entire mass. At one time I thought I had observed that the presence of water favoured the metamorphosis, but I have convinced myself by special experiments that this is not the case. The change takes place as capriciously in the presence as in the absence of water.

It deserves to be noticed that other bodies derived from ethylene by substitution are prone to similar transformations. Thus Regnault,* many years ago, observed analogous phenomena in the case of dichlorinated ethylene.

10. *Iodide of Ethyl.*

The reaction generally used for the preparation of this compound is so simple and elegant, that it would be difficult to propose a better method. Indeed, all the processes which have been suggested differ only as to the proportions of iodine, phosphorus, and alcohol, or as to the manner in which these substances are to be brought into contact with each other. Iodide of ethyl being extensively used as substitution-material in all laboratories, every observation which is calculated to facilitate the preparation of this body may prove acceptable.

The common plan of gradually introducing fragments of phosphorus into the mixture of alcohol and iodine has the disadvantage of occasionally giving rise to powerful reactions, involving considerable loss of materials, even when great care is taken to add the phosphorus slowly and in little fragments. This inconvenience may be readily avoided by introducing the phosphorus, together with about a fourth of the alcohol to be used, into a retort connected with an efficient cooler, into the tubulus of which is fitted a glass globe, provided with tube and stopcock.† The rest of the alcohol is then poured upon the iodine, and the solution thus obtained is introduced through the globe into the retort, which is heated on a sand-bath or in a water-bath. Iodine is but sparingly soluble in alcohol, but excessively so in iodide of ethyl; it is, therefore, only necessary to pour the first portion which distils upon the residuary iodine, which is readily dissolved, and to allow the concentrated iodine solution thus obtained to flow through the globe into the retort, where it is instantaneously converted into iodide of ethyl. This process is especially convenient when the iodide of ethyl is to be prepared on a rather large scale. In this case I find it convenient to dissolve the iodine at once in iodide of ethyl, and to introduce it slowly through the globe into the retort. The stopcock being appropriately adjusted, the process requires but little attention, and, being continuous, yields a very large product in a comparatively limited time. The iodide generally distils at once perfectly colourless, and requires only to be washed with water in order to become free from traces of alcohol. It deserves to be noticed that the process may be carried out in a very moderate-sized retort, since there is only a very limited portion of material at a time under operation.

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* Ann. Chim. Phys. lxix, 151.

† The apparatus used in the preparation of triethylphosphine may be conveniently employed.—Chem. Soc., Qu. J., xi, 60.

Convenient proportions for iodide of ethyl are 1000 grammes of iodine, 700 grammes of alcohol, of spec. grav. 0·84 (83 per cent.), and 50 grammes of phosphorus. From 96 to 98 per cent. of the theoretical quantity of pure iodide of ethyl are obtained. It deserves to be noticed how small a quantity of phosphorus is necessary for the etherification of the iodine, the quantity stated being less than one-half of the amount given in the majority of prescriptions.

Iodide of methyl and iodide of amyl may be prepared in the same manner. In the case of iodide of methyl, the following proportions have been found by experiment to work well. 1000 grammes of iodine, 500 grammes of methylic alcohol (the fraction boiling below 74°), and 60 grammes of phosphorus. The product, owing to the volatility of the compound, is somewhat less than in the previous case, amounting to from 94 to 95 per cent. of the theoretical quantity.

11. *On the deportment of Cyanate of Ethyl with Ethylate of Sodium.*

In a former note[*] I have stated that cyanate of ethyl, when heated with ethylate of sodium, is converted into triethylamine and carbonate of sodium. But I have pointed out at the same time that, owing to the facility with which the ethylate of sodium undergoes decomposition at comparatively moderate temperatures, the process in question appeared to be of limited application.

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[*] Chem. Soc., Qu. J., x, 20.

I have lately had occasion to resume the study of cyanate of phenyl, which I described several years ago.* It appeared to me to be of some interest to apply the above reaction to the preparation of triphenylamine. On performing the experiment, I found, however, that phenylate of sodium and cyanate of phenyl give rise to a different reaction; no triphenylamine was obtained in this process.

This unexpected result induced me to repeat the experiment on the action of ethylate of sodium upon cyanate of ethyl. I have found that in this case likewise the reaction frequently assumes a form different from that which I had previously observed, and which excludes the production of triethylamine. I am engaged in the study of this transformation, the result of which I propose to lay before the Society on some future occasion.

12. *On Glycerin.*

Before the nature of this interesting compound had been finally established by Berthelot's remarkable inquiries, it had been frequently surmised, that the saponification of the several fatty bodies which are found in nature did not invariably furnish the same kind of glycerin.

This view appeared to receive new support in the researches of Wurtz, who has rendered it probable that glycerin is but the type of a class of homologous triatomic alcohols.

As a contribution towards the elucidation of this question, an experiment may be briefly mentioned which arose from a conversation with my friend Mr. George Ferguson Wilson, the technical director of the great establishment well known as Price's Patent Candle Company. Many hundred weights of glycerin are weekly separated in these works, by simple steam-saponification, from a considerable variety of fatty bodies; and Mr. Wilson, who has studied with predilection the preparation and purification of glycerin on a large scale, has acquired a sum of practical information upon this subject such as will not easily be found again. To my question, whether there is more than one kind of glycerin, Mr. Wilson replied, that in his opinion all the fatty bodies which he had examined contained the same variety of glycerin, with the exception of cocoa-nut oil, the glycerin-like constituent of which differed in many respects so much from ordinary glycerin, that he was inclined to consider it as a special variety.

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* Chem. Soc., Qu. J., ii, 323.

Since this question admitted of a simple experimental solution, Mr. Wilson kindly supplied me with a quantity of glycerin obtained by the saponification of cocoa-nut oil. This substance, although prepared in the same manner, differed in colour and odour from the glycerin furnished by other fatty substances. But notwithstanding the colouring matter, and an odorous principle which adhered with great pertinacity, it was not difficult to identify the compound under examination with ordinary glycerin. Distilled with iodide of phosphorus it furnished iodide of allyl, which exhibited the same boiling point as that obtained from ordinary glycerin, and was also transformed under the successive influence of oxalate of silver and ammonia, respectively, into oxalate of allyl and allyl-alcohol.

These experiments appear to solve the question as far as cocoa-nut oil is concerned.

13. *Dinitrotoluic Acid.*

The nitro-substitutes of the aromatic acids are but slowly transformed into dinitro-compounds. Whoever has made the experiment in the benzoyl-series has had an opportunity of experiencing this difficulty. The same remark applies to the toluyl-series: Noad,* to whom we are indebted for the first knowledge of this group, found that nitrotoluic acid may be dissolved in a boiling mixture of nitric and sulphuric acids without undergoing any alteration.

Whilst studying some reduction phenomena of nitro-compounds, I felt an interest in procuring, if possible, a small quantity of dinitrotoluic acid, and by my desire Mr. William Temple has prepared this substance. Pure nitrotoluic acid was digested for two days with three times its weight of equal parts of fuming nitric and sulphuric acids. The solution being mixed with an equal volume of water, a crystallization of dinitrotoluic acid was obtained on cooling. It was washed, recrystallized from water, and submitted to analysis.

I. 0·582 grm. of acid, burnt with oxide of copper, gave 0·908 grm. of carbonic acid and 0·152 grm. of water.

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* Mem. Ch. Soc., III. 437.

II. 0·396 grm. of acid gave 0·614 grm. of carbonic acid and 0·103 grm. of water.

These numbers prove that the acid consisted of dinitrotoluic acid $C_8H_6N_2O_6 = C_8[H_6(NO_2)_2]O_2$ in a state of purity.

	Theory.		Experiment.		
			I.	II.	Mean.
C_8	96	42·48	42·54	42·30	42·42
H_6	6	2·65	2·94	2·88	2·91
N_2	28	12·39	—	—	—
O_6	96	42·48	—	—	—
	226	100·00			

This result is fully confirmed by the analysis of the silver-salt, which is obtained in the form of a white precipitate on addition of nitrate of silver to a solution of dinitrotoluate of ammonium. The silver-salt contains

$$C_8H_5AgN_2O_6 = C_8[H_5(NO_2)_2Ag]O_2.$$

I. 0·609 grm. of silver-salt gave on combustion, 0·643 grm. of carbonic acid and 0·094 grm. of water.

II. 0·130 grm. of silver-salt gave 0·042 grm. of silver.

	Theory.		Experiment.	
			I.	II.
C_8	96	28·83	28·78	—
H_5	5	1·50	1·71	—
Ag	108	32·43	—	32·30
N_2	28	8·41	—	—
O_6	96	28·83	—	—
	333	100·00		

14. *On Isatin.*

Few bodies have fixed the attention of chemists more generally than indigo. But have their experiments led to a satisfactory view regarding the nature of this colouring matter? The brilliant labours of Erdmann and of Laurent have brought to light a rich harvest of the most interesting derivatives of indigo, but they have left us in uncertainty with regard to the constitution of this group of compounds.

With the hope of throwing some light upon this subject, I have endeavoured to eliminate the nitrogen from these compounds by processes likely to act without producing too powerful alterations. The mode of action peculiar to nitrous acid appeared to promise some results; and since indigo, owing to its insolubility, is but little adapted to this reaction, I have made some experiments with isatin, which is so closely allied to indigo.

Supposing isatin to undergo a transformation analogous to that first observed by Piria in similar cases, and consisting arithmetically in the exchange of HN for O, there appeared some hope of obtaining in this manner naphtalic anhydride, and of thus opening a passage from the indigo-group into the naphtalin-series.

Isatin . . .	$C_8H_5NO_2$.
Naphtalic anhydride .	$C_8H_4O_3$.

The history of these two bodies presents some features which conferred a degree of probability on such a transformation. Both isatin and naphtalic anhydride readily assimilate the elements of water, being converted respectively into isatic and naphtalic acids, which, when submitted to the action of alkalies, give both rise to the formation of phenylic derivatives, isatic acid yielding phenylamine, and naphtalic acid being converted into hydride of phenyl (benzol).

Experiment, however, has not confirmed my anticipation, and it might seem superfluous to waste another word upon the subject; nevertheless, I will briefly mention the result of this unsuccessful experiment, since it may probably save some trouble to others.

When studying the deportment of isatin with nitrous acid, I observed the following facts. If finely powdered isatin be suspended in from ten to twenty times its weight of water, and the mixture be then submitted to the action of a current of nitrous acid (disengaged by the action of arsenious acid upon nitric acid, and partially freed from nitric acid by sending it through an empty wash-bottle), the liquid at once begins to effervesce, and the isatin is soon entirely dissolved. The nearly colourless solution invariably contains a considerable quantity of nitric acid generated by the contact of the nitrous acid with the water. To avoid the action of this acid upon the product of the transformation of the isatin, the liquid, mixed with much water, was evaporated upon the water-bath, the water being repeatedly renewed so as to prevent the nitric acid from getting concentrated. The liquid thus evaporated deposited crystals of an acid which, once or twice recrystallized from boiling water, appeared to be perfectly pure.

On analysis the following numbers were obtained—

I. 0·4308 grm. of the acid gave 0·7203 grm. of carbonic acid, and 0·1094 grm. of water.

II. 0·3164 grm. of the acid gave 0·5306 grm. of carbonic acid, and 0·0874 grm. of water.

These numbers lead to the expression,

$$C_7H_5NO_5 = C_7[H_5(NO_2)]O_3,$$

which is the formula of nitrosalicylic (indigotic) acid.

	Theory.		Experiment.	
			I.	II.
C_7	84	45·90	45·60	45·73
H_5	5	2·73	2·81	2·86
N	14	7·65	—	—
O_5	80	43·72	—	—
	183	100·00		

Assuming the nitrosalicylic acid to be a product of oxidation of the body directly formed from isatin under the influence of nitrous acid, the solution before evaporation was neutralized by means of an alkali. The result remained the same. In another experiment, pea-sized pieces of marble were introduced into the mixture of water and isatin before the nitrous acid was passed, in order to remove the free nitric acid as rapidly as it was formed. In these experiments, likewise, nitrosalicylic acid was obtained. It need scarcely be mentioned that the acid derived from isatin possessed all the properties of nitrosalicylic acid prepared by the ordinary method; it exhibited more especially the characteristic coloration with perchloride of iron.

When the liquid obtained by treatment with nitrous acid was evaporated, without having been previously mixed either with water or with an alkali, the isatin, as might have been expected, was transformed into trinitrophenylic acid. This acid was sufficiently characterised by its properties, and by the analysis of its well-known difficultly-soluble potassium-compound.

0·3399 grm. of the potassium-salt, when burnt with chromate of lead, gave 0·3293 grm. of carbonic acid, and 0·0230 grm. of water.

The formula $C_6H_2KN_3O_7 = C_6[H_2(NO_2)_3K]O$ requires the following values,—

	Theory.		Experiment.
C_6	72	26·97	27·14
H_2	2	0·75	0·76
K	39	14·60	—
N_3	42	15·73	—
O_7	112	41·95	—
	267	100·00	

15. *Spontaneous Decomposition of Gun-cotton.*

Some gun-cotton prepared in the establishment of Messrs. Hall, soon after Schönbein's discovery, and taken out of a cartridge intended for blasting, had been preserved by my friend Dr. Percy since 1847, in a glass bottle provided with a glass stopper. After some time, red vapours had appeared in the interior of the bottle, and the cotton had crumbled down to a loose powder. When lately the bottle was again examined, the powder was found to be converted into a light brown, semi-fluid, gum-like mass, while the side of the bottle had become coated with a net-work of fine needles. It was not difficult to collect a sufficient quantity of these crystals; they exhibited all the characters of oxalic acid. In order to fix their nature by a number, they were converted, first into the ammonium-salt, and then into the silver-salt.

0·2420 grm. of silver-salt gave 0·2275 grm. of chloride of silver = 70·74 p.c. of silver.

Oxalate of silver contains 71·05 p.c. of silver.

The viscid mass into which the bulk of the gun-cotton had been converted, exhibited all the properties of ordinary gum; it was likewise interspersed with crystals of oxalic acid.

16. *Experimental illustration of the Composition of Ammonia in Lectures.*

The decomposition of ammonia by the spark-current, exhibits in a conspicuous manner the condensation which accompanies the transformation of a mixture of hydrogen and nitrogen into ammonia. It is more difficult to illustrate the relative proportion of the nitrogen and hydrogen which exists in ammonia. The following experiment elucidates, though indirectly, this relation.

A glass tube from 30 to 40 inches in length, and $\frac{3}{4}$ of an inch in width, is sealed at one end and divided without particular care into three equal parts, which are conveniently marked by paper or by india-rubber rings. The tube is then filled over water with pure chlorine, and at once transferred into a test-glass half filled with mercury and half with concentrated solution of ammonia. In this manner a layer of ammonia one or two inches in height, and separated from the bulk of the liquid by mercury, is collected in the tube. A lively reaction immediately sets in, the mercury rises, and the ammonia-solution floating on the metal effervesces, with evolution of nitrogen, while the chlorine disappears, dense white clouds of chloride of ammonium being formed.

According to the equation—

$$H_3N + 3Cl = 3HCl + N,$$

the 3 volumes of chlorine should be replaced by 1 volume of nitrogen, and this result is actually observed. At the common temperature, however, the reaction is but slowly accomplished, the disengagement of nitrogen from the solution of ammonia becoming slower and slower, but often continuing for hours. On the other hand, the decomposition is instantaneous if the tube be gently inclined, and the liquid floating upon the mercury be heated to ebullition. To complete the experiment it is only necessary to transfer the glass tube into a high cylinder filled with water, in which the inner and outer liquids may become level when the 3 volumes of chlorine originally filling the tube, are found to be very accurately replaced by 1 volume of nitrogen gas.

Supposing the composition by volume of hydrochloric acid to be known, the composition of ammonia is fixed by this observation. The experiment furnishes moreover an instructive illustration of the volume-equivalence of chlorine, hydrogen, and nitrogen.

17. *How to exhibit the Inflammability of Ammonia.*

It is well known that ammoniacal gas cannot be inflamed in atmospheric air, but will burn in oxygen gas with a greenish-yellow flame. This flame may be shown by allowing the gas to issue from a bent jet into a vessel containing oxygen. There is, however, some difficulty in lighting the gas, and under the most favourable circumstances the phenomenon is very ephemeral. To avoid this inconvenience, the inflammability of ammonia is generally exhibited by sending a current of the gas into an ordinary flame, the ammonia-gas being allowed to issue from the delivery tube into the lower opening of an Argand gas-burner provided with a glass chimney. The gas burning low and almost invisibly, the high lambent ammonia-flame becomes very conspicuous.

The phenomenon may, however, be observed in a purer and much more brilliant form, when a wide-mouthed flask, containing a strong aqueous solution of ammonia is heated upon a sand-bath, and a rapid current of oxygen gas from a gas-holder forced through the boiling liquid. The mixture of oxygen and ammonia-gas thus formed may be lighted, and burns at the mouth of the flask with the characteristic greenish-yellow flame, which continues until the ammonia is expelled from the liquid.

18. *Separation of Cadmium from Copper.*

Having had occasion to perform some experiments on the relative merits of the several processes which have been suggested for the separation of cadmium from copper, I was led to observe a property of sulphide of cadmium, which I do not find noticed in analytical manuals. Sulphide of cadmium dissolves with the greatest facility in boiling dilute sulphuric acid, which has no effect upon the sulphide of copper. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part of concentrated sulphuric acid and 5 parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow sulphide of cadmium. Another solution of the same composition was mixed with an excess of cyanide of potassium and treated with sulphuretted hydrogen gas. A distinct yellow coloration was observed: a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in cyanide of potassium also gives rise to a yellow coloration, when submitted to the action of sulphuretted hydrogen.

19. *Separation of Arsenic from Antimony.*

The separation of these two metals, which presents unusual difficulties, has been a task of predilection with chemists, and a great number of processes have been suggested, the majority of which, it cannot be denied, admit of improvement. Among the many methods, the one which is based upon the dissimilar deportment of arsenetted and antimonetted hydrogen with nitrate of silver, deserves to be favourably mentioned, the former, as is well known, yielding arsenious acid which passes in solution:

$$H_3As + 6AgNO_3 + 2H_2O = 6HNO_3 + 6Ag + HAsO_2.$$

the latter giving rise to the formation of antimonide of silver:

$$H_3Sb + 3\ AgNO_3 = 3HNO_3 + Ag_3Sb$$

which is insoluble in water. This process presents no difficulty as far as the arsenic is concerned, which may be recognized in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. It is far less easy to find, according to this process, minute quantities of antimony in the presence of large quantities of arsenic, the silver-compound of antimony being mixed with a bulky precipitate of metallic silver. By treating this precipitate, as might readily suggest itself, with hydrochloric acid, there dissolves, together with antimony, a small quantity of chloride of silver, which is sufficient to darken the precipitate produced in the solution by sulphuretted hydrogen to such a degree as altogether to mask the presence of antimony. This inconvenience may easily be obviated by boiling the mixture of silver and antimonide of silver, after the arsenious acid has been carefully washed out by boiling water, with *tartaric acid,* which dissolves the antimony alone. The solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

In some experiments made with the view of testing the delicacy of this process, 1 part of antimony in presence of 199 parts of arsenic, and *vice versâ,* 1 part of arsenic, together with 199 parts of antimony, could be easily detected. Even with minute quantities the process proved successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other could be satisfactorily exhibited. In evolving the hydrogen-compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases.

If there be tin with the arsenic and antimony, this metal will be deposited upon the plates of zinc used in evolving the hydrogen, from which it may be mechanically detached, dissolved in hydrochloric acid, and tested by the usual processes.

20. *Analysis of the Saline Water of Christian Malford, near Chippenham.*

The water used for analysis, was collected November 11, 1858.

The water pumped up from the well is perfectly clear and colourless, and almost inodorous. It has a distinctly saline taste, and effervesces on agitation, exhibiting the presence of a considerable quantity of free carbonic acid. The water contains, in addition to carbonic acid, a minute trace of an inflammable carbonetted hydrogen. The presence of the latter becomes perceptible if a considerable quantity of the water be heated to ebullition, and the gases expelled be passed through a solution of potassa. The gas not absorbed is a mixture of atmospheric air with the carbonetted hydrogen; it burns, owing to the preponderance of the air, with a pale scarcely visible flame. On standing, more readily on boiling, the water deposits a yellowish sediment, consisting of carbonate of calcium, carbonate of magnesium, sesquioxide of iron, and organic matter.

Temperature of the water 12°C, the temperature of the air being nearly the same.

Specific gravity of the water = 1·006.

The analysis was performed in the usual manner; only the determination of the bromine requires a passing notice.

In determining this element, I have availed myself of the method of imperfect precipitation. According to the observations of Lyte and of Field, nitrate of silver produces in a mixture of chloride, bromide, and iodide, a precipitate, first of iodide, and then of bromide, and a precipitate of chloride only after the whole of the iodine and bromine have been separated;—a method of separating chlorine, bromine, and iodine, based upon this deportment, has been proposed by the latter chemist.

The amount of iodine present in the water of Christian Malford, is so exceedingly small, that the quantitative determination appeared useless. The task was, therefore, limited to the determination of the bromine.

For this purpose, 28 litres of the water were evaporated to dryness, and the saline residue was exhausted with dilute alcohol. The alcoholic liquid, when submitted to distillation, left a saline mass, which was dissolved in a small quantity of water. This solution was measured and divided into two equal parts, each of which represented the extract of the saline residue of 14 litres = 14084 grammes of the original water, containing the whole of the bromides and part of the chlorides. Each of the liquids thus obtained was precipitated by a silver-solution, containing 0·4288 grammes of pure silver, whereby the whole of the bromine, and part of the chlorine was thrown down. The two precipitates weighed respectively 0·6355 (I), and 0·6350 (II) grammes.

If P represent the weight of the mixed precipitate, and x the amount of chloride of silver in it, then $P-x$ is the quantity of bromide of silver, and if the total amount of the silver in the precipitate be represented by S, then

$$S = \frac{108}{143 \cdot 5} x + \frac{108}{188} (P - x)$$

whence

$$x = \frac{S - 0 \cdot 5745 P}{0 \cdot 1781}.$$

By substituting the experimental values for S and P in the above expression, we find

	I.	II.
Chloride and bromide of silver (by experiment)	0·6355	0·6350
Chloride of silver (by calculation)	0·3576	0·3593
Bromide of silver	0·2779	0·2757
Corresponding (in 14084 grms. of water) to bromine . . .	0·1182	0·1173
Or in 1000 grms. to	0·0084	0·0083

Direct results of analysis calculated to 1000 grammes of water.

a. BASES.

Experiment.	Sesquioxide of Iron.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.	0·0035	0·4234	0·1897	6·9600	0·863	6·097
II.	0·0035	0·4241	0·1903	6·8800	0·897	5·983
Mean....	0·0035	0·4238	0·1900	6·9200	0·880	6·040

b. ACIDS

(or elements replacing them).

Exp.	Sulphuric Acid.	Chlorine.	Bromine, with traces of Iodine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid combined as Carbonate of Calcium and Magnesium.	Carbonic Acid free.
I.	0·2464	4·5630	0·0084	0·0150	0·2921	0·1050	0·1871
II.	0·2452	4·5570	0·0083	0·0145	0·3164	0·1072	0·2092
Mean ..	0·2458	4·5600	0·0084	0·0148	0·3043	0·1061	0·1982

c. RESIDUE LEFT ON EVAPORATION.

Experiment.	Mineral Residue.	Organic Matter.	Total Residue.
I.	8·2000	0·0200	8·2200
II.	8·1900	0·0200	8·2100
Mean	8·1950	0·0200	8·2150

VERIFICATIONS.

a. VERIFICATION FOR LIME.

Experiment.	Lime precipitated on ebullition. (Carbonate of Calcium.)	Lime left in solution after ebullition. (Sulphate and Chloride of Calcium.)	Total by Calculation.	Total by Experiment
I.	0·1285	0·2895	0·4180	0·4284
II.	0·1307	0·2856	0·4163	0·4241
Mean	0·1296	0·2876	0·4172	0·4238

b. VERIFICATION FOR MAGNESIA.

Experiment.	Magnesia precipitated on ebullition. (Carbonate of Magnesium.)	Magnesia left in solution after ebullition. (Chloride of Magnesium.)	Total by Calculation.	Total by Experiment.
I.	0·0022	0·1852	0·1874	0·1897
II.	0·0025	0·1863	0·1888	0·1903
Mean	0·0024	0·1857	0·1881	0·1900

SALINE CONSTITUENTS.

	In 1000 grammes of water.	In one gallon, (70,000 grains) of water.
	Grammes.	Grains.
Sulphate of calcium	0·4179	29·253
Carbonate of calcium . . .	0·2314	16·198
Chloride of calcium	0·2289	16·023
Carbonate of magnesium . .	0·0050	0·350
Chloride of magnesium . .	0·4413	30·891
Bromide of magnesium (with traces of iodide of magnesium)	0·0096	0·672
Carbonate of iron	0·0051	0·357
Chloride of potassium . .	0·8800	61·600
Chloride of sodium	6·0400	422·800
Silica	0·0148	1·036
Organic matter	0 0200	1·400
	8·2940	580·580

The water contains 29·02 cubic inches in the gallon, or 104·6 cubic centimetres in the litre, of free carbonic acid. The quantity of carbonic acid was determined at the well. It deserves to be mentioned that the water for this purpose was pumped up, whereby probably a minute quantity of gas was lost.

My thanks are due to Mr. E. Millar, of Christian Malford, for his help in collecting the water, and to Dr. Leibius for his assistance in performing the experiments.

21. *Spontaneous Decomposition of Chloride of Lime.*

One morning (I think it was in the summer of 1858), when entering my laboratory, which I had left in perfect order on the previous evening, I was surprised to find the room in the greatest confusion. Broken bottles and fragments of apparatus lay about, several window panes were smashed, and all the tables and shelves were covered with a dense layer of white dust. The latter was soon found to be chloride of lime, and furnished without difficulty the explanation of this strange appearance.

At the conclusion of the Great Exhibition of 1851, M. Kuhlmann, of Lille, had made me a present of the splendid collection of chemical preparations which he had contributed. The beautiful large bottles were for a long time kept as a collection; gradually, however, their contents proved too great a temptation, and in the course of time all the substances had been consumed. Only one large bottle, of about 10 litres capacity, and filled with chloride of lime, had resisted all attacks; the stopper had stuck so fast that nobody could get it out; and after many unsuccessful efforts—no one venturing to indulge in strong measures with the handsome vessel—the bottle had at last found a place on one of the highest shelves of the laboratory, where for years it had remained lost in dust and oblivion, until it had forced itself back on our recollection by so energetic an appeal. The explosion had been so violent that the neck of the bottle was projected into the area, where it was found with the stopper still firmly cemented into it.

I have not been able to learn whether similar cases of the spontaneous decomposition of chloride of lime have been already observed.

22. *Bisulphide of Carbon in Coal Gas.*

It is well known that coal gas, even when submitted to the most improved processes of purification, retains a minute quantity of a sulphur-compound, which yields sulphurous acid when the gas is burned. A commission having been appointed for the purpose of reporting* to the Lords of the Committee of Privy Council on Education on the lighting of picture-galleries by gas, and on any precautions (if necessary) against the escape of gas and of the products of its combustion, the writer of this note undertook a few experiments, with the view of determining the amount of sulphur generally present in the London coal gas.

The object of the inquiry being to ascertain the quantity of sulphurous acid capable of being formed by the combustion of the gas, an exceedingly small jet of gas, carefully washed with acetate of lead—which showed the absence of sulphuretted hydrogen—and measured by an accurate experimental meter, was burned in a large two-necked glass globe. Through one of the necks the gas tube was conveyed into the globe, whilst the other, fitting into a condenser, carried off the product of combustion into a two-necked receiver. To establish a current of air, the receiver was connected with a water-current aspirator, a couple of Woolfe's bottles containing water or dilute ammonia being inserted, for the purpose of fixing any trace of sulphurous acid which might escape condensation, with the water, in the receiver. The experiment being terminated, the liquids in the receiver and in the wash-bottles were united, oxidized with chlorine and precipitated with chloride of barium.

Experiments in July, 1859.

Order of Experiments.	Quantity of Gas consumed.	Amount of Sulphate of Barium.	Amount of Sulphur in 100 cubic feet.		Amount of Sulphur in 100 cubic metres.
	Cubic feet.	Grammes.	Grammes.	Grains.	Grammes.
I.	1·98	0·0630	0·437	6·74	15·433
II.	2	0·0840	0·577	8·90	20·371
III.	2	0·0630	0·433	6·68	15·278
IV.	2	0·0740	0·508	7·84	17·944
Mean	..	..	0·488	7·54	17·256

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* Report on the subject of Lighting Picture Galleries by Gas, by Professors Faraday, Hofmann, and Tyndall, Mr. Redgrave, R.A, and Capt. Fowke, R.E,

Experiments in December, 1859, and January, 1860.

Order of Experiments.	Quantity of Gas consumed. Cubic feet.	Amount of Sulphate of Barium. Grammes.	Amount of Sulphur in 100 cubic feet.		Amount of Sulphur in 100 cubic metres. Grammes.
			Grammes.	Grains.	
V.	2	0·0890	0·611	9·43	21·585
VI.	2	0·0953	0·654	10·10	23·111
VII.	2	0·0975	0·669	10·33	23·644
VIII.	2	0·0935	0·642	9·91	22·677
Mean	..	..	0·644	9·94	22·754

These experiments show that the amount of sulphur remaining in the London gas after the removal of the sulphuretted hydrogen is very small, and that in winter it is somewhat greater than in summer. This may possibly arise from the enormously increased production of gas during the winter months, when it will be more difficult to regulate the several processes involved in its manufacture. But the result may also be purely accidental, arising from a change in the nature of the coal used, etc. A much more extended series of experiments would be required to decide this question.

It has long been assumed that the sulphur in purified gas exists in the form of bisulphide of carbon, the conditions for the generation of this compound being in fact given in the ordinary process of producing gas. That coal gas really contains bisulphide of carbon was first elegantly proved by Vogel,* who, at the suggestion of Baron Liebig, passed a current of purified gas through an alcoholic solution of potassa, when xanthate (sulphocarbonate) of potassium ($K(C_2H_5)CS_2O$) was formed, which produced in copper-solutions the highly characteristic yellow precipitate of xanthate of copper, and yielded, when boiled with a few drops of nitrate of lead in the presence of free potassa, a black deposit of sulphide of lead. When engaged in the above inquiry, I repeated Vogel's experiments, which I can confirm in every particular. The amount of bisulphide of carbon in the London gas is, however, so small, that a very large volume must be passed through the alcoholic solution of potassa in order to produce a sufficient quantity of xanthate of potassium. After a cubic foot of gas had been passed through alcoholic potassa in a bulb apparatus, the solution gave with sulphate of copper a leek-green precipitate, in which the presence of xanthate was but imperfectly indicated. Only after passing several additional cubic feet the yellow colour became more distinct, although still masked to some extent by the hydrated protoxyde simultaneously precipitated. On the other hand, the black precipitate of sulphide of lead was obtained without difficulty, even after the passage of one single cubic foot of gas.

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* Liebig's Annalen lxxxviii, 369.

But the presence of bisulphide of carbon in coal gas may be exhibited even more elegantly, and with greater precision, by means of *triethylphosphine*, which produces with the bisulphide a compound crystallizing in splendid prisms of a ruby colour. This body is so characteristic, and forms with so much facility, that bisulphide of carbon has become a most valuable re-agent for triethylphosphine and its homologues. The idea naturally suggested itself to employ the phosphorous-base for the detection of bisulphide of carbon in gas. On distilling a considerable proportion of coal-gas-benzol, I had separately collected a small fraction, which came over in the commencement below 65°. When mixed with triethylphosphine, this liquid solidified into a mass of the well known ruby crystals. Four or five drops of triethylphosphine were dissolved in ether, the ethereal liquid was introduced into a bulb apparatus, and a current of coal gas allowed to bubble through the solution. When 0·2 of a cubic foot had passed, the liquid had assumed a distinctly red coloration, the intensity of which increased as the passage of the gas and the evaporation of the ether continued. After 0·8 of a cubic foot had passed, the whole of the ether had evaporated, and the inner surface of the bulb-apparatus was lined with a beautiful network of the ruby crystals.

23. *Remarks on the Changes of Gutta Percha under Tropical Influences.*

[From a Report addressed to Sir W. B. O'Shaughnessy, Director-General of Telegraphs in India.]

The peculiar change which gutta percha undergoes when in contact with air for some time is well known, this substance gradually becoming brittle, and ultimately losing all coherence. This effect was experienced on an undesirable scale in construct-ing the East Indian Telegraphs. Enormous quantities of gutta percha, became in a comparatively short time, entirely useless, involving a loss of thousands of pounds. At the request of Sir W. B. O'Shaughnessy I have made a few experiments with the gutta percha thus altered, the results of which were recalled to my mind by the researches on the alteration of gutta percha lately published by Oudeman. It may be of some interest briefly to mention the analytical results furnished by the changed material submitted to me for examination.

The specimens sent home from India formed a brown, exceedingly brittle substance, softening to a plastic mass in boiling water. Since the gutta percha existing in commerce does not always exhibit the same characters, it was of some importance for the inquiry, that a quantity of the original unchanged substance, with which the wires sent out to India had been coated, was likewise placed at my disposal. In their deportment with solvents the changed and unchanged gutta percha exhibited a marked difference. Whilst the latter proved to be perfectly insoluble in strong alcohol, the changed gutta percha was in a great measure taken up by this solvent. By treating the changed material first with cold, then with boiling alcohol, and ultimately with ether, three substances were obtained, which, although very much alike in their physical properties, differed considerably from each other in their chemical composition.

I.—*Substance soluble in cold Alcohol.*

Cold alcohol readily attacked the outer surface of the coating, and dissolved a considerable portion. On evaporation a brown resinous mass remained behind, which was dried, first over sulphuric acid, and ultimately at 100°; at which temperature it readily fused. The fused mass solidified on cooling to a brittle substance, yielding a highly electrical powder, and exhibiting on combustion the following percentage composition.

	I.	II.	Mean.
Carbon	62·94	62·64	62·79
Hydrogen . . .	9·22	9·36	9·29
Oxygen. . . .	27·84	28·00	27·92
	100·00	100·00	100·00

II.—*Substance soluble in boiling Alcohol.*

By treating with boiling alcohol the residue of the previous operation, which had ceased to yield anything more to cold alcohol, a fresh quantity of substance was obtained in solution. The alcoholic liquid, on evaporation, left a residue very similar to that of the previous operation, which, when dried in the same manner, furnished on analysis the following numbers.

	I.	II.	Mean.
Carbon	68·13	67·29	67·72
Hydrogen . . .	10·01	10·18	10·09
Oxygen	21·86	22·53	22·19
	100·00	100·00	100·00

III.—*Substance insoluble in cold and in boiling Alcohol.*

The residue left after repeated treatment with boiling alcohol, dissolved in ether, a few mechanical impurities remaining behind. The ethereal solution gave with alcohol a precipitate which dried up to a yellowish powder, becoming highly electrical by trituration, and caking when gently heated. It had the general characters of gutta percha, being merely somewhat deeper coloured and less plastic. When analysed, it furnished numbers nearly agreeing with those which were obtained by several observers for gutta percha.

Carbon	88·12
Hydrogen	12·49

The body last analysed was obviously unchanged gutta percha; a view which is also supported by its solubility in chloroform and benzol. The substance in question differed from specimens of gutta percha investigated by others, and especially from that which Payen considers the pure gutta percha, by its solubility in ether. The original substance with which the wires had been coated was, however, likewise soluble in ether. It cannot, therefore, be doubted that gutta percha exists in several modifications.

The experiments which I have quoted prove that the changes which gutta percha undergoes in contact with air depend upon oxidation. Unchanged gutta percha is free from oxygen; the product dissolved by cold alcohol contained nearly 28 per cent., and that soluble in boiling alcohol still more than 22 per cent. of oxygen.

I need not mention that I am far from believing that these oxygenated substances are definite chemical compounds. Their mode of preparation altogether precludes such an idea, the object of the experiments having been simply to establish the fact of oxidation having taken place. That the changes of gutta percha are due to the absorption of oxygen, is countenanced by the experience of this substance having been kept for years under water without undergoing any alteration.

On the Carbonates of Alumina, Ferric Oxide, and Chromic Oxide.

By James Barratt, Esq.

(*Abstract.*)[*]

The composition of the precipitate produced in solutions of sulphate or chloride of aluminium by alkaline carbonates has been variously stated as follows :—According to

Muspratt (Chem. Soc. Qu. J. ii. 216),	it is	$3Al_2O_3 . 2CO_2 + 4HO$
H. Rose (Pogg. Ann. xci. 452)	„	$Al_2O_3 . 3HO + NH_4.CO_2 + HO$
Langlois (Ann. Ch. Phys. [3] xlviii. 502)	„	$8Al_2O_3 . CO_2 + 8HO$
Wallace (Chem. Gaz. 1858, 410)	„	$3Al_2 . 2CO_2 + 9HO$

From experiments made by the author of this paper in Dr. Muspratt's laboratory, it appears that the precipitate formed by carbonate of soda in a solution of chloride of aluminium (the mode of preparation adopted by Wallace), after being washed and dried, then triturated with water, again washed, and dried over sulphuric acid, consists of hydrate of alumina perfectly free from carbonic acid, a result which agrees with the statement of Saussure (Gmelin's Handbook, iii. 308.)

Carbonate of Chromic Oxide has been analysed by several chemists. According to

Berzelius (Traité, iv., 427),	it is	$4Cr_2O_3 . CO_2 + 3HO$
Meissner (Gilb. Ann. lx. 366)	„	$10Cr_2O_3 . 7CO_2 + 8HO$
Langlois (loc. cit.)	„	$2Cr_2O_3 . CO_2 + 6HO$
Lefort (Compt. rend. xxvii. 269) Wallace (loc. cit.)	„	$Cr_2O_3 . CO_2 + 4HO$

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[*] This paper is published *in full* in the Chemical News, No. 10, p. 110.

Mr. Barratt's experiments confirm the result obtained by Lefort and Wallace.

Carbonate of Ferric Oxide.—Soubeiran (Ann. Ch. Phys. [2] xliv. 326) found that the precipitate thrown down by alkaline carbonates from *ferrous* salts, after thorough washing and exposure to the moist air of a cellar for six months, no longer contains ferrous oxide, but consists of 71·4 p.c. Fe_2O_3, 8·3CO_2 and 20·0 water ($3Fe_2O_3.CO_2+12HO$). According to Langlois (loc. cit.), the precipitate formed by alkaline carbonates in ferric salts, contains, when dried at 100° C., 81·47 p.c. Fe_2O_3, 10·17 HO, and 1·36 CO_2, which is given off at 165°. L. Gmelin (Handb. v. 222), on the contrary, states that this precipitate, after thorough washing, is quite free from carbonic acid. According to Wallace (loc. cit.), the precipitate thrown down by carbonate of ammonia from ferric chloride, contains, when dried in the air at 22° to 24° C., $3Fe_2O_3.CO_2+6HO$, and gives off 2 eq. water at 100°; and the precipitate formed by carbonate of soda in a solution of ferric nitrate is $9Fe_2O_3.CO_2+12HO$.

Mr. Barratt finds that the precipitate dried in the air at ordinary temperatures contains $3Fe_2O_3.CO_2+8HO$, half of the water being expelled at 100° C.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 19, 1860.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

Charles A. Cameron, M.D., Dublin; Charles Henry Wood, Esq., 17, Bloomsbury-square; August Dupré, Ph.D., 53, Burton-crescent; William Plunket, Esq., Museum of Irish Industry, Dublin.

The following papers were read:—

"On refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of coinage," by Mr. Robert Warrington.

"On certain sources of loss of precious Metal in some operations of assaying," by Mr. G. H. Makins.

"On the double Sulphides of Iron and Copper," by Mr. F. Field.

February 2, 1860.

Dr. H. Bence Jones, Vice-President, in the Chair.

Edward Divers, Esq., Queen's College, Galway, and Edwin Crocker, Esq., 19, Richmond-road, Barnsbury, were elected Fellows of the Society.

The following papers were read:—

"On an Iron Sand from New Zealand," by Dr. J. H. Gladstone.

"On the composition of Air from Mont Blanc," by Dr. E. Frankland.
"On Biniodacetic Acid," by Messrs. Perkin and Duppa.

February 16, 1860.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

Frederick Dupré, Ph.D., 53, Burton-crescent; Dr. Edward Smith, 6, Queen Ann-street, Cavendish-square; Edward Nicholson, Esq., St. Mary's Hospital, Paddington.

A paper was read "On some derivatives from the Olefines," by Dr. Guthrie.
Dr. Odling made a verbal communication "On the direct Oxidation of Chlorhydric Acid."

March 1, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

Messrs. Berthelot, Deville, Frémy, Fritzsche, Peligot, and Mulder, were elected Foreign Members.

George Morley, Esq., 18, Park-place, Leeds, was elected a Fellow of the Society.

The following papers were read:—

"On New Zealand Iron Sand," by Mr. E. Riley.
"On the action of Chloride of Ethyl upon Ammonia," by Mr. Groves.

March 15, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

The following papers were read:—

"On the composition of the Platinidcyanides," by Mr. Hadow.

"On a new Ammonio-chrome Compound," by Mr. Morland.

"On the analysis of a Water from the superficial strata of the London basin," by Mr. Hooker.

Anniversary Meeting, March 30, 1860.

Professor Brodie, President, in the Chair.

The Report of the Council, and the Audited Account of the Treasurer, were read.

Messrs. Crookes and Morland having been appointed Scrutators, the Meeting proceeded to the election of Council and Officers for the ensuing year, and the following were declared to have been duly elected:—

President.—B. C. Brodie, F.R.S.

Vice-Presidents, who have filled the office of President.—W. T. Brande, F.R.S.; C. G. B. Daubeny, M.D., F.R.S.; Thomas Graham, F.R.S.; W. A. Miller, M.D., F.R.S.; Lyon Playfair, Ph.D., F.R.S.; Colonel Philip Yorke, F.R.S.

Vice-Presidents.—E. Frankland, Ph.D., F.R.S.; H. Bence Jones, M.D., F.R.S.; Robert Porrett, F.R.S.; Alfred Smee, F.R.S.

Secretaries. — Theophilus Redwood, Ph.D.; William Odling, M.B., F.R.S.

Foreign Secretary.—A. W. Hofmann, LL.D., F.R.S.

Treasurer.—Warren De La Rue, Ph.D., F.R.S.

Other Members of Council.—Frederick Field; William Francis, Ph.D., F.L.S.; G. D. Longstaff, M.D.; Dr. Marcet, F.R.S.; John Mercer, F.R.S.; Henry M. Noad, Ph.D., F.R.S.; A. R. Normandy, A.R.L.M.; H. E. Roscoe, Ph.D.; Edward Schunck, Ph.D.; J. A. Voelcker, Ph.D.; Robert Warington; A. W. Williamson, Ph.D.; F.R.S.

It was resolved—

That the thanks of the Meeting be given to the President, Officers, and Council, for their services during the past year.

That the thanks of the Meeting be given the Auditors for their services to the Society.

The following donations have been received:—

"Repertory of Arts and Manufactures:"
"Repertory of Patent Inventions:"
"London Journal of Patent Inventions:"
Carpmael's "Law of Patents of Invention:"
Carpmael's "Law Reports of Patent Cases:"
from Messrs. De La Rue and Co.

"Quarterly Journal of the Geological Society," Part 1, for 1860: from the Society.

"Pharmaceutical Journal" for January, February, March, 1860: from the Editors.

"Chemical News," Nos. 1 to 16: from the Publishers.

"Journal of the Society of Arts," Vol. VIII., Nos. 372 to 384: from the Society.

"Journal of the Photographic Society" for January, February, March, 1860: from the Society.

"Literary Gazette," Vol. IV., Nos. 80 to 92: from the Publisher.

"Monthly Notices of the Royal Astronomical Society," Vol. XX., Nos. 1 to 6: from the Society.

"Canadian Journal" for March, 1860: from the Canadian Institute.

"American Journal of Science and Arts," January, 1860: from the Editors.

"Journal of the Franklin Institute," January, February, 1860: from the Institute.

"Proceedings of the Academy of Natural Sciences of Philadelphia," 1860, No. 1—5: from the Academy.

"Note on some Numerical relations between the Specific Gravities of the Diamond, Graphite, and Charcoal Forms of Carbon, and its Atomic Weight:" by Dr. Lyon Playfair: from the Author.

"On the Hardness of Metals and their Alloys;" and "On the Specific Gravities of Alloys; by F. C. Calvert and R. Johnson: from the Authors.

"Annales de Chimie" (1789 to 1805), 55 volumes: from Dr. R. D. Thomson.

"Mélanges physiques et chimiques tirés du Bulletin physico-mathématique de l'Académie de St. Petersbourg," Tomes I., II., III.: from the Academy.

"Annuaire de l'Académie royale des Sciences des Lettres et des Beaux Arts de Belgique, 1859."

"Bulletin de l'Académie royale, &c., de Belgique, 1859":
from the Academy.

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt in Wien, 1859," Nos. 2, 3: from the Institute.

"Öfversigt af kongl. Vetenskaps Akademiens Förhandlingar, 1858": from the Academy of Sciences of Stockholm.

THE

QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY.

IX.—*On certain sources of loss of Precious Metal in some operations of Assaying.*

BY G. H. MAKINS.

IN the assay of specimens of alloyed gold, the degree of heat used in the first operation, viz., cupellation (when this is carefully performed), is usually somewhat varied, according to presupposed proportions in the alloy,—for example, a much lower temperature being sufficient where the gold is only associated with silver, than where it is also mixed with oxidisable metals, which latter have to be separated entirely by this first operation.

About five years since, I chanced to have before me some 200 assays of gold, wherein the silver also had to be estimated, and in which, for other reasons, an extraordinary degree of heat was required to be employed; and as I made simultaneously with these, several synthetical proofs, I was much struck by the great extent of loss of gold and silver; and satisfied that it could not be entirely due to what is known amongst assayers as cupel absorption, I determined upon examining some of the contents of an iron flue of a cupel furnace, which passed from its hood into a chimney, in order to see if gold had been volatilized along with other metals, and if so, to what extent.

A quantity of apparently carbonaceous matter was therefore taken out of it; and as this flue was at the time recently put up afresh, I had the means of knowing that it had been used for the cupellation of gold assays only.

Upon examination of this material by the microscope under an inch power, it exhibited very distinctly portions of oxide of lead, in yellow masses, little nodules of suboxide of copper, minute grains of silver, together with portions resembling silver reduced from chloride,—the whole mixed with a quantity of carbonized matter containing small grains of unburnt fuel.

From pressure of business at the time, this material was laid aside (after cursory examination sufficient to prove the presence of the metals), until it could be completely examined. This was not done, however, until after the appearance of some collateral matter, communicated to the Society by my late pupil, Mr. Napier.

On further examination, the metallic matters present were found to consist of oxide of lead mixed with small portions of gold, silver, and oxide of copper; and as my object was only to estimate the gold and silver present, I took separate portions, viz., two of 50, and two of 100 grains each. They were each treated with 400 grains of pure lead, that is to say, with eight times the weight of the former two, and four times the latter, each having also its own weight of borax added.

The mixtures were then scorified, and the operation carried to its full extent, so as to diminish as much as possible the quantity of lead for the subsequent cupel process.

The process completed, the specimens were poured in a good fluid condition; the slag (which was quite free from metallic beads) separated; and the resulting metal next subjected to cupellation.

The little buttons so obtained, consisting of pure silver and gold, were then weighed.

From the first two assays (the material operated upon being 100 grains), the resulting buttons weighed (after compensating for silver contained in the lead employed), just ·089 grain.

From the second two, upon 200 grains, the buttons weighed ·166. If we average these, which are very nearly alike, and calculate the quantity for 1000 grains, we should have a result of ·850 grain.

They were next all parted for gold, and the result was ·026; equal to ·087 in every 1000 grains.

Deducting then the weight of this gold from the weight of the compound metal, we find the quantity of the precious metals in 1000 grains to be,

Gold ..	·087
Silver ..	·763

Of course I do not attempt to establish any ratio between these quantities and an individual assay; for although the flue whence this material was taken had only been renewed a few months, yet during that time the fumes of many thousand assays had passed through it. But, on the other hand, I would remark, that considering that this flue is removed daily when the furnace is at work, the proportion which the precious metals bear to the whole, is very large indeed.

I will now call attention to a second cause of loss of gold occurring in parting operations, and possibly also in refining upon the large scale, viz., the solution of a portion of gold in the nitric acid used, although the latter is pure and quite free from hydrochloric acid.

Berzelius, in speaking of this fact says, "It must not be forgotten that if nitric acid contains hydrochloric or *nitrous* acid, it will dissolve gold; in truth, the quantity dissolved is inconsiderable in the latter case, but sufficient to lead to an incorrect result." Now, in parting gold by nitric acid, we are generating during the operation quantities of nitrous acid, and consequently have the conditions present for this loss to take place.

Some time since, Mr. Field (the Queen's Assay Master), had in his office a pear-shaped bottle, into which nitric acid was constantly being poured after parting operations: it was thickly coated with gold. He showed this to Sir J. Herschell, who was then Master of the Mint, asserting that it was deposited from an actual solution of the gold. The latter gentleman supposed rather that it was a deposit from mechanically suspended particles; but this could have hardly been the case, as the bottle was a large pear-shaped one, and the gold coated the upper part as thickly as the lower, and very uniformly, which certainly could not have been the case had it been simply a deposit of mechanically suspended particles. It was no doubt, as Mr. Field observed, a good example of deposit from an actual solution.

I tried the following experiment, in order to arrive at some idea of the quantity so taken up in ordinary assaying operations.

Four assay-quantities of pure gold were accurately weighed, then added to the usual proportion of fine silver, and of lead, and cupelled. The buttons then rolled and coiled, were parted with nitric acid. For the boilings, acids were prepared of specific gravity 1·25 and 1·35 respectively.

No. 1 assay was then boiled 20 minutes in the weaker, and afterwards for 13 minutes in the stronger acid, between which operations the cornet was washed with hot distilled water.

No. 2 assay was boiled once in the first, and twice in the second acid.

No. 3. Once in the first, and three times in the second.

And No. 4. Once in the first, and four times in the second; the boilings, as I have said, being continued for 20 minutes in the weak, and for 13 minutes in the second acid.

The several cornets were then washed off with hot distilled water, annealed, and weighed, and the following is the result:—

Calling the weighings before the operations 1000: the first cornet weighed 999·6, the second 992, the third 998·7, and the fourth, 997·9; the loss thus increasing in proportion as we multiply the number of boilings.

Now, the question occurs as to whence the loss arises. I may first say, that it has been suggested that it is due to silver being more completely separated by the repeated boilings.

But in reply to this I can state, that I have examined these cornets over and over again; and that after the first boiling as above described, the amount of silver left in them is very uniformly 1·16 in the 1000 parts. But the difference between 999·6, the weight of the first cornet, and 997·9, that of the fourth, is 1·70; here then, supposing the latter to be entirely free from silver (which is not really the case), we have 0·54 abstracted, a quantity just equal to 3 grains in the troy pound, which loss can only be traced to the removal of gold.

Next: it has been urged, that the appearance of gold in the used parting acid, is due to mechanical causes, dependent upon the friction of an exceedingly soft and spongy body, by its being thrown violently about in a dense acid fluid, and by the rapid evolution of bubbles of acid, or acid vapour, rushing from its surface, all this being of course increased as the density of the acid is increased by evaporation.

I believe that this is not the case, and that in the fluid medium no such abrasion takes place, but that it is a true case of solution, and by the agency of the nitrous acid evolved. In proof of this I have taken a portion of this acid which had been so used, and after dilution, separated the silver, then evaporated, and obtained small quantities of gold, which were next redissolved in nitro-hydrochloric acid, and proved to be such by the usual tests.

Again, I do not think that the deposit upon Mr. Field's store bottles (to which I have alluded), could have taken place in so regular a manner upon their upper portions without actual solution; for had it been mere mechanical suspension, the metal upon the lower part would of course have been much in excess.

Now, as to the evolution of this nitrous acid. At the first boiling, when the silver is present in such large quantity, nitrous acid is given off most copiously; but probably its solvent action upon the gold is then controlled and checked by electrical action, that is, by the gold becoming the negative, and the silver the positive element in a voltaic circuit; but when the silver is wholly (or nearly) removed, this check no longer exists, and the solution of the gold progresses more rapidly.

Then, with respect to the cause of the evolution of nitrous acid,—of course as I have already said, as long as there is any silver to oxidise, it will be generated; and when the silver is nearly abstracted, the method of boiling adopted by many assayers induces its continuance; for it is scarcely possible to boil an assay in strong acid without some means of disengaging the vapour formed; if some help be not afforded, the acid will "bump" so much as almost, if not quite, to throw it out of the flask. Hence it is the custom with some to introduce a small portion of charcoal, which, from its porosity, tends to the steady evolution of this vapour. Now, if the charcoal be entirely carbonized, it does not materially affect the acid; but if it contain much woody matter not thoroughly carbonized, it is then sure to decompose it, and set nitrous acid free. Indeed, I have for some years ceased to use this body, from its injurious effects upon the acid.

I am aware that the matters mentioned in this paper are somewhat trivial in a scientific point of view; but their commercial importance will be at once admitted, when we remember the enormous values dealt with in this country, and consider, moreover, that they are at times turned over and over again and that the question of profit and loss in such commercial operations are much, if not entirely, in the hands of the assayer.

Lastly, this publication may serve to account for some of the discrepancies which are sometimes found between assayers.

X.—*On Bibromosuccinic Acid and the Artificial Production of Tartaric Acid.*

By W. H. Perkin, F.C.S., and B. F. Duppa, Esq.

In April of last year, we published a paper on the action of pentachloride of phosphorus on malic acid,[*] in which we stated that there seemed reasons for believing that there existed a close relation between succinic, malic, and tartaric acids, similar to that which exists between acetic, glycollic, and glyoxylic acids; and for the purpose of verifying that supposition, we proposed endeavouring to obtain mono- and bibromo-succinic acids, thinking that by hydrating them by means of hydrate of silver, or by decomposing their silver-salts in the presence of water, we might obtain malic and tartaric acids. Since that time, we have obtained both of these bromo-acids, but up to the present have only studied the bibromosuccinic acid.

Bibromosuccinic Acid.

We endeavoured to produce this substance by the direct action of bromine on succinic acid, but did not obtain any satisfactory results. The process by which we have succeeded in obtaining this acid, is as follows:

Equal volumes of bromine and chloride of succinyl are heated in a strong sealed tube to a temperature of 120 or 130°C. for three or four hours. The tube, after having cooled, must be very carefully opened, so that the hydrobromic acid which has formed may slowly issue forth; if the tube be opened too rapidly, its contents will be projected and lost. The product thus obtained is an oily liquid consisting of impure chloride of bibromosuccinyl. This is decomposed by being well agitated for an hour or two with two or three times its volume of water, after which, the liquid will contain considerable quantities of the new acid in the form of a crystalline precipitate; this is purified by being well washed on a filter to separate hydrochloric acid, and also another extremely soluble acid which has been formed. It is then dissolved in a moderately strong solution of carbonate of sodium and filtered for the purpose of removing a small quantity of an oily substance. The resulting sodium salt is then decomposed by nitric acid, which causes the new product to separate as a crystalline precipitate, which, when thoroughly washed on a filter with cold water and then dried, constitutes pure bibromosuccinic acid.

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[*] Phil. Mag. April 1859.

Carbon, hydrogen, and bromine determinations of specimens dried in vacuo over sulphuric acid, gave the following numbers:—

I. ·4150 of substance, gave
·2643 of carbonic acid and
·0600 of water.

II. ·2950 of substance, gave
·4035 of bromide of silver.

Percentage composition:—

	I.	II.
Carbon . .	17·36	—
Hydrogen .	1·60	—
Bromine . .	—	58·2

which agree with the formula,

$$C_8\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right\}O_8$$

as may be seen from the following table:—

		Theory.		Experiment.
Carbon	8 equiv. . .	48	17·39	17·36
Hydrogen	4 „ . .	4	1·44	1·60
Bromine	2 „ . .	160	57·97	58·20
Oxygen	8 „ . .	64	23·20	——
		276	100·00	

Bibromosuccinic acid is difficultly soluble in cold, but tolerably so in hot water, from which it crystallises on cooling in opaque prisms; it is very soluble in alcohol and extremely so in ether. We have found the latter solvent very useful in separating small quantities of this acid from its aqueous solutions. Crystals of bibromacetic acid decrepitate when gently heated, but when subjected to a high temperature, decompose with formation of hydrobromic acid. It has a strong acid taste and reddens litmus rapidly. We have but cursorily examined the salts of this acid.

Bibromosuccinate of sodium is very soluble and appears to contain water of crystallisation.

Acid *bibromosuccinate of potassium* is a white crystalline salt sparingly soluble.

Bibromosuccinate of silver is obtained by adding a solution of nitrate of silver to either of the above salts. It is a white salt nearly insoluble in water. The following determinations were made of a specimen dried over sulphuric acid in vacuo :—

I. ·5316 of substance, gave
·1879 of carbonic acid and
·0288 of water.

II. ·4163 of substance, gave
·2418 of chloride of silver and
·3195 of bromide.

These results agree with the theoretical numbers, as may be seen by the following table :—

		Theory.		Experiment.
Carbon	8 equiv.	48	9·79	9.63
Hydrogen	2 ,,	2	·40	·60
Bromine	2 ,,	160	44·08	43·71
Silver	2 ,,	216	32·65	32·64
Oxygen	8 ,,	64	13·08	——
		490	100·00	

On boiling a quantity of bibromosuccinate of silver with water, it gradually decomposes, with evolution of carbonic acid and formation of bromide of silver; the ebullition must be continued until no more carbonic gas is evolved. The resulting mixture is then thrown on a filter; the less soluble portion, which consists chiefly of bromide of silver, is well washed with water; and to the filtrate which contains a small quantity of silver in solution, a few drops of hydrochloric acid are added. The liquid is then separated from the chloride of silver by means of a filter, and evaporated on a water bath, until of a syrupy consistence. After remaining at rest for four and twenty hours under a bell-jar over sulphuric acid, it is found to contain a considerable quantity of large crystals, which are then separated from the residual syrupy acid by washing rapidly with cold alcohol; the product thus obtained is *tartaric acid.*

A portion of this acid was dissolved in water and divided into two equal quantities. One of these was neutralized with carbonate of potassium, and then the other added to it, which caused the well-known precipitate of the acid tartrate of potassium to form, whereof we made the following carbon, hydrogen, and potassium determinations:—

I. ·202 grm. of substance, gave
·18875 grm. of carbonic acid and
·0540 of water.

II. ·205 grm. of substance, gave
·19200 grm. of carbonic acid and
·0500 of water.

III. ·1545 grm. of substance, gave
·0590 of chloride of potassium.

Percentage composition:—

	I.	II.	III.
Carbon	25·49	25·5	—
Hydrogen	2·9	2·7	—
Potassium	—	—	20·0

These numbers agree very closely with the theoretical, as may be seen by the subjoined table:—

		Theory.		Experiment.
Carbon	8 equiv.	48	25·60	25·49
Hydrogen	5 „	5	2·65	2·80
Potassium	1 „	39·2	20·00	20·0
Oxygen	12 „	96	51·75	——
		188·2	100·00	

This interesting formation of tartaric acid may be thus explained:

$$\underset{\text{Bibromosuccinate of Silver.}}{\underline{\left.\begin{matrix}(C_8H_2Br_2O_4)''''\\ \quad Ag\end{matrix}\right\}O_4}} + 2\,H_2O_2 = \underset{\text{Tartaric Acid.}}{\underline{\left.\begin{matrix}(C_8H_2O_4)''''\\ \quad H_4\end{matrix}\right\}O_8}} + 2\,Ag\,Br;$$

evidently showing that it is derived from four molecules of water.

We have alluded to a syrupy acid which is formed at the same time as tartaric acid, and from which it had to be separated by means of cold alcohol. This we have not investigated, as its nature shows that it would be very difficult to obtain pure, and consequently would require considerable quantities, which, coupled with the expense and labour of obtaining only a few grammes of bibromosuccinic acid, has induced us to lay this part of the investigation aside for the present. It seems, however, probable that it is *pyruvic acid*; which, it will be remembered, is formed from tartaric acid by the loss of carbonic acid and water; and may it not be possible that part of the tartaric acid, at the moment of formation, splits up into carbonic acid, water, and pyruvic acid?

We are now investigating monobromosuccinic acid, from which we expect to obtain some interesting results.

XI.—*On the Composition of the Platinidcyanides.*

BY EDWARD A. HADOW, ESQ.

As the platinidcyanides are derived from the platinocyanides, it will be well briefly to mention, in the first place, the mode of formation and properties of the latter. The platinocyanides are a remarkable set of salts belonging to the stable class of double cyanides, exceeding the ferrocyanides in the force with which they retain the electro-negative metal and disguise it to ordinary tests. Concentrated and boiling nitric or hydrochloric acids, alone or mixed, extract no platinum from them; they are unaffected by digestion with peroxide of mercury, and concentrated boiling sulphuric acid liberates cyanide of platinum with difficulty only. They have the general formula MCy.PtCy or $MPtCy_2$, the platinum in them existing in the state corresponding to protochloride of platinum, so that, before preparing these salts from a solution of bichloride of platinum, it must be reduced to the condition of protochloride, either by sulphurous acid, or by evaporation to dryness and expulsion of half the chlorine by heat. The product in either case is treated with excess of cyanide of potassium until a clear solution is obtained, which, if previously warm and sufficiently concentrated, will deposit on cooling, long prisms of the potassium-salt, from which the other platinocyanides may easily be derived, by precipitating its solution with that of a salt of copper, washing the precipitate, suspending it in water, and decomposing it by a current of sulphuretted hydrogen; the solution which contains hydroplatinocyanic acid, and, after filtration from the sulphide of copper, may be saturated with any required base. A more convenient way I find, in many cases, is to treat the protochloride of platinum directly with the required base, and sufficient hydrocyanic acid to form the double cyanide; the combination takes place easily if assisted by a gentle heat, and it is only necessary to crystallise a few times to get rid of the chloride present in the solution.

These salts are remarkable for the great beauty and variety of the colours their crystals exhibit, while their solutions are transparent and colourless. The platinocyanide of magnesium is, perhaps, the most beautiful of these salts; it forms by slow evaporation large and regular prisms of a deep red by transmitted light, but viewed by reflected light the sides of the prisms exhibit a brilliant beetle-green, and the extremities a deep blue or purple colour. The red salt gently warmed, even under water, becomes bright yellow, which is also the colour of crystals deposited from a solution at a temperature of 160 °F.; heated to 212° F. the salt becomes quite white, and again at a higher temperature bright yellow. These changes of colour correspond to successive losses of water, the ordinary red salt containing 7 equiv.; the yellow, according to Weselsky, 6 equiv. At 212° F. the salt still retains 2 equiv., which are only expelled by a heat of between 300° and 400°, when it becomes anhydrous and again yellow. If a portion of this yellow anhydrous salt be laid on the red salt in powder, it will soon abstract water (from the latter), and a white layer will be formed between two yellow borders, one of these yellow compounds being anhydrous, and the other containing 6 equiv. of water. In endeavouring to prepare this salt, I, on one occasion, made use of a method given by Quadrat, which consists in evaporating to dryness mixed solutions of sulphate of magnesia and platinocyanide of potassium, and digesting the dried mass in a mixture of alcohol and ether; instead of which, however, I used only alcohol, and that somewhat weak, and by so doing obtained a solution, which gave, in addition to the ordinary dark red salt, another set of crystals of a paler red, and exhibiting a steel-blue lustre by reflected light, instead of the usual emerald-green of the ordinary salt. Analysis proved it to be a double platinocyanide of magnesium and potassium, having the formula

$$MgPtCy_2 . KPtCy_2 + 2HO + 5aq = 416{\cdot}5.$$

	Calculated.	Found.	
$2Pt$ =	47·54	47·2 – 47·1	
$4Cy$ =	24·97	—	
Mg =	3·00	3·02	
K =	9·36	9·41	
$2HO$ =	4·32	4·40	expelled above 212° F.
$5HO$ =	10·81	10·97	expelled at 212.
	100·00		

In this, as in many other platinocyanides, a portion of water is retained at 212°. This salt cannot be recrystallised except from a considerable excess of platinocyanide of magnesium, and even when this is present, sudden cooling, or agitation of the saturated solution, causes the separation of the potassium salt free from magnesium.

These platinocyanides, represented by the general formula $MPtCy_2$, may be transformed into the salts termed platinidcyanides, by the action of chlorine, bromine, nitric acid, &c.—a set of compounds characterised in the crystalline form by a peculiar coppery lustre, and to which the general formula $M_2Pt_2Cy_5$ has hitherto been assigned. They are thus represented as differing from the platinocyanides by the addition of an atom of cyanogen to every two atoms of the latter salts.

$$Mg_2Pt_2Cy_5 = 2(MgPtCy_2) . Cy.$$

This somewhat improbable formula seemed yet to be strongly confirmed by the following facts. Gerhardt at first doubted it, but afterwards confirmed it by an analysis of the potassium-salt. A determination of the platinum and potassium made by myself agreed so closely with the requirements of the formula as also strongly to confirm it. These salts act like the ferridcyanides in presence of a free alkali,—exerting a powerful bleaching action on cochineal; they also liberate iodine from iodide of potassium, confirming the analogy between the two sets of salts. They evolve cyanogen when heated sufficiently, leaving a residue of platinocyanide. They are produced equally by the action of bromine, nitric acid, and other oxidizing agents on the platinocyanides, showing that no single one of these is essentially necessary for their formation.

But then, on the other hand, the following difficulties presented themselves. The platinum and basic metal remain in the same proportion to each other in the platinidcyanides as in the platinocyanides from which they are derived, the difference being merely an excess of cyanogen in the latter over that in the former. Whence is this cyanogen derived? In the case of the ferridcyanides, the proportion between the iron and the basic metal in the ferrocyanide has been altered by the chlorine, which abstracts a portion of the basic metal, leaving the cyanogen behind to explain the excess found in the ferridcyanide:

$$2(M_2FeCy_3) + Cl = M_3Fe_2Cy_6 + MCl.$$

But to account for that in the platinidcyanides, it is necessary to assume the simultaneous removal, by the action of chlorine on the platinocyanides, of equal proportions of platinum and basic metal:

$$3(MPtCy_2) + Cl = M_2Pt_2Cy_5 + MCl + PtCy;$$

an explanation which appears very improbable to any one who has observed the great stability of the platinocyanides, and the remarkable ease with which the transformation by chlorine occurs. These salts, it is true, have an oxidizing effect in presence of potash, in consequence of which, by the addition of an oxidizable body, they are reduced to platinocyanides; but then it ought to occur with simultaneous formation of free cyanide of potassium:

$$M_2Pt_2Cy_5 + KO + X = 2(MPtCy_2) + KCy + XO,$$

but no free cyanide can be detected as a product of such a reaction in any case. Moreover, there exists another salt, the ultimate product of the action of chlorine on the platinidcyanide of potassium (the salt chiefly examined), usually represented by the formula $PtCy_2.KCl$, the formation of which from the platinidcyanide is equally difficult of explanation with that of the latter from the platinocyanide; and further still is it difficult to represent the mode of the reduction of the chlorinated salt to the state of platinidcyanide, which, however, actually occurs very readily under the action of reducing agents.

The determination of the proportions between the cyanogen and the platinum at once served to clear up most of these difficulties. The proportion was found to be identically the same in the platinidcyanides as in the platinocyanides; and the difference between the two sets of salts in composition was found to consist in the addition of a certain amount of the chlorine, bromine, or other elementary or compound salt-radical used for their formation,—so that there exist, not one set, but many sets of platinidcyanides, requiring the prefix of *chloro*, *bromo*, &c., to distinguish them. Such being the case, it appeared most probable that Knop's and Gerhardt's salts had been true cyano-platinocyanides, as the above formula indicates, formed under some peculiar conditions, perhaps in presence of excess of cyanide of potassium, so that cyanogen, instead of chlorine, had really been superadded to the original platinocyanide, and that the salt under examination differed from theirs only in containing chlorine in place of cyanogen. I was therefore not a little surprised to find, instead of 1 atom of chlorine to 2 atoms of platinum, which a chlorine-compound analogous to this cyanogen-compound should contain, not above a third of that quantity; accordingly, even if the chlorine ever were truly replaced by cyanogen—which, after several attempts, I failed to effect—the formula $M_2Pt_2Cy_5$ never could represent the composition of the cyano-platinocyanides, the superadded cyanogen being too large in amount by two-thirds.

Considerable difficulty was found in determining the amount of chlorine in the salts, on account of their high atomic weight. Repeated combustions of the chloro-platinocyanide of potassium with nitrate of potash and carbonate of soda gave a proportion of 1 equiv. of chlorine to between 6 and 7 equiv. of platinum. This analytical method proving unsatisfactory, from not giving a probable formula, a synthetical method was tried, with better success; it was found that a solution of platinocyanide acidulated with hydrochloric acid, rapidly and perfectly decolorises a solution of permanganate of potash, until the platinocyanide has taken up the maximum amount of chlorine, and become converted into the salt, $PtCy_2KCl$, which has been before mentioned as the ultimate product of the action of chlorine on the chloro-platinocyanides, and which might be termed the perchloro-platinocyanide of potassium. As no method could be devised to indicate when the first stage of the change, namely, from platinocyanide into chloro-platinocyanide, is complete, it was not possible to determine the amount of chlorine necessary for its formation in this direct way; but, starting from the chloro-platinocyanide, it was easy to determine by means of permanganate of potash how much *additional* chlorine was necessary to convert it into the perchloro-platinocyanide, the true composition of which had been determined and found to have been correctly represented in its elementary proportions by the formula hitherto given. It was thus found that while 6 equiv. of the platinocyanide, containing 6 equiv. of platinum, required 6 of chlorine for the formation of the perchloro-platinocyanide, a quantity of the chloro-platinocyanide, containing the same amount of platinum, required only 5 equiv. of chlorine to convert it into the same salt, proving that 1 equiv. already existed in this quantity of the salt, and, therefore, that its true composition in the anhydrous state is $6(KPtCy_2)Cl$. This composition explains its oxidizing power in alkaline solutions, and why no free cyanide can be detected when its force has been spent on an oxidisable body:

$$6(KPtCy_2)Cl + KO + X = 6(KPtCy_2) + KCl + XO,$$

an alkaline chloride, and not a cyanide, being formed. The evolution of cyanogen, and its reduction to platinocyanide when heated, is due to the chlorine partly entering the salt, and displacing cyanogen; (a certain amount of chloride of ammonium is however likewise formed at the time when moisture is present):

$$6(KPtCy_2)Cl = 5(KPtCy_2) + KCl + PtCy + Cy.$$

The salt after this gives a somewhat turbid solution, from PtCy which has been set free. The formation of the salt from the platinocyanide, and its ready conversion into the perchloro-platinocyanide, and the reduction of the latter into the chloro-platinocyanide and platinocyanide successively, by reducing agents, is due to the successive additions of chlorine in one case, and successive abstractions of it in the other, without any formation or separation of cyanide of platinum, or of chloride of potassium, in either case—

$$6(KPtCy_2) + Cl = K_6Pt_6Cy_{12}Cl$$
$$K_6Pt_6Cy_{12}Cl + 5Cl = 6(KPtCy_2Cl).$$

The chloro-platinocyanide of potassium, as ordinarily dried in a hot-water oven, loses the percentage of water given by Gerhardt in his analysis, but still retains 3 equiv., which, together with the chlorine overlooked, correspond pretty nearly in weight with the excess of cyanogen supposed to exist in the salt, and which thus appears to have been determined by difference only. The composition of the crystallised salt is:

$$Pt_6K_6Cy_{12}.Cl + 3HO + 18aq = 1364·5.$$

The direct determinations of chlorine, as before stated, were unsatisfactory, inasmuch as they showed on the average a deficiency of about 0·20 per cent. The salt has a slight tendency to lose water of crystallisation in dry weather. The water was therefore determined in two samples, one dried spontaneously in the air, the other by strong pressure in bibulous paper immediately after removal from its solution, as the two extremes to furnish a correct mean.

		Air-dried.		Dried by Pressure.	Average.	Calculated for 18HO.
18HO	Loss per cent at 212° =	11·34	10·9	12·34	11·53	11·87
3HO	„ 400° =	1·94	1·97	—	1·96	1·98

Composition of salt dried at 212°:—

		Found.		Average.	Calculated.
6Pt	= 49·27	50·07	48·7	49·34	49·39
6K	= 19·68	—	19·92	19·80	19·47
12Cy	= 25·83	—	—	25·83	25·95
Cl	= 2·76	2·82	2·79	2·79	2·95
3HO	= 2·19	2·23	—	2·21	2·24
				99·97	100·00

The quantities of the salt taken for the various determinations varied from 7 to 13 grs. The platinum and potassium were obtained by evaporation with pure concentrated sulphuric acid, followed by gentle ignition. The cyanogen was determined by combustion of 10·6 grs. with soda-lime.

The above formula represents the empirical composition of the chloro-platinocyanide of potassium. Its true rational composition was discovered on precipitating its solution with a solution of zinc, when it was found to have resolved itself into a platinocyanide, which was precipitated in combination with zinc, and a perchloro-platinocyanide, which remained in solution; and, accordingly, on mixing a solution of the perchloro-platinocyanide, a salt which forms large colourless crystals, with another of the nearly colourless platinocyanide, the mixture, if sufficiently concentrated, will deposit immediately an abundant crop of copper-coloured crystals of chloro-platinocyanide:

$$5(KPtCy_2) + KPtCy_2Cl = K_6Pt_6Cy_{12}Cl.$$

It appears, in fact, to be a double salt of the two.

The solution, accordingly, of the so-called platinidcyanides exhibits the reactions of a mixture of its component salts, and it is thus impossible by any direct tests to ascertain whether either is in excess or not; this point can only be determined by careful crystallisation. By this latter method the formula of the chloro-platinocyanides was further confirmed; the two component salts were mixed in various proportions, and the compound salt was crystallised out, when one or other of its components would be found in excess, unless the right proportions had been taken. The results obtained in this way were not absolutely satisfactory, in consequence of partial decomposition during repeated crystallisation; but they served to counterbalance the determinations of chlorine by analysis, the errors in the numbers obtained being in the opposite direction, and indicating the proportion of 1 equiv. of chlorine to between 5 and 6 equiv. of platinum. It was found that, from whatever solution the chloro-platinocyanide was crystallised, it always contained the same amount of chlorine, so that there appears to be no double salt intermediate between the chloro-platinocyanide and perchloro-platinocyanide; and, accordingly, if a purely cyanogen-platinocyanide existed, it may be concluded from analogy that it would have the composition,

$$5(PtKCy_2) + PtKCy_3 \text{ and not } (PtKCy_2 + PtKCy_3)$$

which the hitherto accepted formula requires. The bromo- and nitro-platinidcyanides so closely resemble the corresponding chlorinated salts as hitherto to have been confounded with them under the general term of platinidcyanides, and as their appearance and facility of formation are so much alike, there is every reason to conclude that they have an analogous composition, being, in fact, double salts of a platinocyanide, and a corresponding perbromo- and pernitro-platinidcyanide, which, like the highest chlorine compounds, are colourless. In the case of nitric acid, NO_6 must represent the chlorine and bromine of the corresponding salts. There appear to be no analogous iodine compounds, since any one of these salts treated with iodide of potassium immediately liberates iodine. But there are analogous compounds containing the salt radical SO_4 in place of chlorine, bromine, &c., and, doubtless, similar compounds with the salt-radicals of other acids; the existence of the sulphuric compound was inferred in the first instance from finding that a solution of a platinocyanide acidulated with sulphuric acid rapidly decolorises a permanganate. The crystallised oxysulpho-platinocyanide of potassium is readily obtained by adding a little peroxide of lead to a saturated solution of platinocyanide of potassium acidulated with sulphuric acid;—each particle of peroxide dropped in becomes instantly enveloped in a moss-like growing mass of the copper-coloured salt.

From a few experiments recently made, it would appear that these remarkable compounds may also be regarded as salts in which the platinocyanide $MPtCy_2$ plays the part of a metal, since, in the sulphuric compound, the sulphuric acid readily admits of replacement by another acid by double decomposition with a baryta-salt; and, accordingly, it seems to be not unlikely that there are oxygen-compounds capable of acting the part of bases, and combining directly with acids to form the per-compounds which by combination with the platinocyanides, form the platinidcyanides. It is on account of the feeble affinity that exists between the platinocyanide (as a compound metal) and the salt-radical, that reducing agents so readily decompose them into the platinocyanide and the corresponding acid, just as they would the corresponding salts of gold, the gold being supposed to represent the platinocyanide in its feebly electro-positive character. If sulphuretted hydrogen be passed into their solutions, which are neutral, they immediately become strongly acid.

The most distinctive reactions between the platinocyanides and perchloro-platinocyanides, are that the former give an abundant *smalt-blue* precipitate with nitrate of suboxide of mercury, and a *flocculent* blue precipitate with salts of copper. The latter give a *white* with nitrate of suboxide of mercury, and a fine *sandy* blue with salts of copper; they liberate iodine from iodides; and if dropped in the solid form into a concentrated solution of platinocyanide of potassium, they are immediately coated with copper-coloured needles.

The platinidcyanides in solution exhibit both sets of reactions, and accordingly, cannot be distinguished until crystallised out, when their dark coppery lustre at once characterizes them. The neatest way of forming the chlorine and bromine salts at once in a state of purity is, to take a concentrated solution of a platinocyanide, measure off a sixth-part and convert it by an excess of chlorine or bromine into the perchloro- or perbromo-platinocyanide, expelling the excess of the chlorine and bromine subsequently by a gentle heat, and then adding the remaining five-sixths of platinocyanide; in a very short time the double salt will form abundantly in a state of perfect purity.

XII.—*On the Stibethyls and Stibmethyls.*

By G. B. Buckton, Esq., F.R.S.

Chemists are already aware, through the researches of Dr. Hofmann, that zinc-ethyl reacts on terchloride of antimony in a manner similar to that shown by terchloride of phosphorus;—in the former case, triethylstibine is formed, in the latter case, triethylphosphine. The same successful labourer in this field of chemical inquiry, in his profound and complete history of ammonia, lately communicated to the Chemical Society, groups these bodies as primary triamines, or ammonias in which antimony and phosphorus severally play the parts of nitrogen, and three equivalents of ethyl those of hydrogen.

The following experiments were undertaken with the intention of testing how far the compounds of antimony with methyl and ethyl, were limited to the ammonia-type, and more particularly to determine whether, by assimilating more than three molecules of methyl, &c., bodies might arise referable to the types of antimonious and antimonic acids.

Triethylstibine is known to combine with two equivalents of chlorine or iodine to form its haloïd salts. If substitution could be effected, through zinc-ethyl, in these substances, a pentethylated radical would arise, showing the antimony in a complete condition of saturation.

Coarsely powdered antimony attacks iodide of ethyl readily, when sealed in tubes, and exposed to a temperature of about 140° C. An oily liquid is formed, composed of biniodide of triethylstibine, with probably a little teriodide of antimony. This biniodide, $Sb(C_4H_5)_3I_2$, produces considerable heat when mixed with zinc-ethyl, a pasty mass being formed, upon the surface of which a yellowish liquid floats. Distillation is attended by an abundant evolution of inflammable gas, which is charged with the vapour of triethylstibine. To remove as far as possible the inconvenience of these dense white antimonial fumes, the first distillation is best performed in a quilled receiver, the tube of which is plunged into water.

The yellowish heavy liquid, obtained as above, was rectified in an atmosphere of coal gas.

The first portion contained a little ether, which was separated, after which the temperature rose to 150°, between which and 170° C. all the liquid products passed over.

The fraction boiling below 160° C. had the properties of triethylstibine, but gave numbers slightly higher than those required by theory.

	Theory.		Experiment.	
Sb	129	59·73	—	—
C_{12}	72	33·33	33·51	33·97
H_{15}	15	6·94	7·17	7·39
	216	100·00		

Triethylstibine, when pure, is a colourless and limpid fluid, having a faint odour, which can scarcely be styled alliaceous. An unpleasant and very persistent taste is left in the mouth when a small portion only of its vapour has been inhaled. It is spontaneously inflammable in air, but may be kept unchanged under a layer of water. It mixes with bromine, under water, without disengaging any noticeable quantity of gas, and the oily bibromide of triethylstibine is formed. With hydrochloric acid hydrogen gas is liberated, and the corresponding non-fuming bichloride is produced.

Triethylstibine is a very stable body, and distils without change. Here it differs from Stanethyl, which, as Dr. Frankland has shown, deposits when heated, half its quantity of tin, and passes into stannic diethyl.

Lowig and Schweitzer found the boiling point of triethylstibine to be 159° C.

A combustion of the samples boiling between 160° and 170° C., showed a considerable increase in the percentage of both carbon and hydrogen.

Although the numbers obtained, approach more nearly the composition of tetrethylstibine than that of pentethylstibine, it is thought more probable that the latter substance is really contained in the mixture. The percentage of carbon and hydrogen was not increased by another rectification of the sample, and it soon became evident that the body was broken up by heat. This observation furnishes an explanation of the copious liberation of gas noticed during the distillation of biniodide of triethylstibine with zinc-ethyl.

Tetrethylstibine.			Sample 1.		Sample 2.	
Sb	129	52·65	—	—	—	—
C_{16}	96	39·19	37·51	37·44	35·96	35·44
H_{20}	20	8·16	7·90	8·01	7·43	7·39
	245	100·00				

The decomposition of such a body by heat is analogous to that of pentachloride of antimony, which is thus known to yield chlorine gas and the terchloride. In the same manner,

$$Sb(C_4H_5)_5 = Sb(C_4H_5)_3 + C_4H_4 + C_4H_5H.$$

The existence of a stibium compound, containing more than three molecules of ethyl, was confirmed by the deportment of the sample under examination towards bromine. A portion of the fuming liquid was thrown up into the head of an eudiometer tube standing over mercury, and small quantities of bromine were introduced from time to time. The mixture was attended with a violent action, and a bulk of permanent gas was formed. As the neutral point was approached, all visible action ceased, but when the bromine was in slight excess, a partial absorption of gas was noticed.

As triethylstibine unites with bromine to form the bibromide without liberation of gas, the appearance of ethylene and hydride of ethyl can only be explained by the presence of a more complex ethylated radical than triethylstibine.

The absorption of gas also would thus be easily explained.

$$Sb(C_4H_5)_5 + 4Br = Sb(C_4H_5)_3Br_2 + C_4H_4Br_2 + C_4H_5H.$$

Triethylstibine passes into the non-fuming bichloride also more readily with concentrated hydrochloric acid than the substance here described, which loses its character of spontaneous inflammability only after long boiling.

It is remarkable that zinc-ethyl is not attacked by bichloride of triethylstibine, even when the mixture is raised to its boiling point.

The most characteristic salt of triethylstibine is the bisulphide, which is easily formed by heating the radical with alcohol and sulphur. It crystallises in long silky needles, which are readily soluble in water. This salt is rapidly decomposed by boiling in excess of aqueous cyanide of potassium. The cyanide is in this manner converted into sulphocyanide of potassium, and triethylstibine is liberated in white fumes.

If the mixture containing the higher stibium-radical be boiled with alcohol and sulphur, there is formed, together with bisulphide of triethylstibine, a considerable quantity of bisulphide of ethyl. This substance becomes immediately evident by its powerful and repulsive odour.

Although triethylstibine is remarkably persistent in itself, its salts are in general easily reduced.

The most convenient method of obtaining the radical triethylstibine is by distilling its salts with granulated zinc. As the biniodide is easily formed, it is well suited for such an operation. The action is set up with some energy, and the products are most conveniently received under water.

I have failed in forming substitution-products by bringing together triethylstibine and bisulphide of carbon. The same failure also has happened in my attempts to cause a reaction between triethylstibine and bibromide of ethylene. An interesting body from triethylphosphine, homologous to sulphocarbamate of ammonium, has been obtained by Hofmann:

$$2\,PE_3 + C_2S_4 = (C_2S_2)''\left.\begin{matrix}E_2P\\E_4P\end{matrix}\right\}S_2.$$

With triethylstibine the tubes invariably burst at a temperature of 140° C., and below this point no change appeared in the materials.

Having some quantity of triethylstibine at my disposal, a few experiments in confirmation of those of M. Löwig were made.

On the Salts of Tetrethylstibine.

Triethylstibine was mixed with a slight excess of iodide of ethyl. In the course of a few hours, a mass of fine crystals of iodide of tetrethylstibine was obtained.

Iodide of tetrethylstibine, when mixed with zinc-ethyl and distilled, yields the same results as if biniodide of triethylstibine had been employed. Iodide of zinc, fixed gases, and a mixture of two radicals incapable of separation by heat were obtained.

Oxide of Tetrethylstibine is very soluble in water, and is uncrystallizable. When heated above 100° C. it undergoes decomposition, with liberation of white fumes of triethylstibine.

Sulphate and nitrate of tetrethylstibine are crystalline salts.

Chloride of Tetrethylstibine is also crystalline. When dissolved in water, and mixed with bichloride of platinum, it yielded a fine yellow crystalline salt, which was but little soluble in alcohol.

When ignited and separated from the antimony, the following analytical result was obtained.

0·7856 grm. of salt, gave 0·1752 grm. of platinum, which accords most nearly to the formula,

$$Sb(C_4H_5)_4Cl.PtCl_2$$

	Theory requires.		Found.
Sb . .	129·0	28·63	—
C_{16} . .	96·0	21·30	—
H_{20} . .	20·0	4·44	—
Cl_3 . .	106·5	23·65	—
Pt . .	99·0	21·98	22·31
	450·5	100·00	

Löwig obtained a salt much richer in platinum, to which he assigns the composition,

$$3PtCl_2,\ 2(Sb(C_4\ H_5)_4Cl).$$

Action of Zinc-methyl on Biniodide of Trimethystibine.

As the methyl-molecule is simpler in structure than that of ethyl, it was thought that a penta-methylated body might possibly resist decomposition during distillation. The biniodide of trimethylstibine may be obtained in beautiful crystals, by acting on metallic antimony with iodide of methyl, at a temperature of 140° C. As these crystals were found to decompose zinc-methyl energetically, an appeal was again made to experiment.

The materials were mixed slowly in a retort, and after the first action had subsided, the mass was submitted to a temperature of 100° in a water-bath, which removed the excess of zinc-methyl and ether. Subsequently, the distillation of the solid mass was completed over the sand bath.

In this way, a heavy pale-coloured liquid was obtained, which, after agitation with water and weak acid, was rectified in an atmosphere of coal gas, heat being applied by a water-bath.

Fractions were taken between 80°—86°, 86°—96°, 96°—100° C.

All these samples had the following properties:

They were oily bodies with faint odours, heavier than water, with which they did not mix. When exposed to the air, they were not spontaneously inflammable, neither did they, at ordinary temperatures, give off white fumes. When dropped on a warm surface, however, they ignited and burnt with a luminous flame, accompanied by a dense antimonial cloud.

The following numbers were obtained by analysis of these samples:—

	80°—86°		86°—96°	96°—100°	
Carbon . .	21·99	21·20	26·90	30·18	31·64
Hydrogen .	5·08	5·23	5·92	6·83	6·98

For comparison, the numbers required by theory for antimony with three, four, and five equivalents of methyl, are appended.

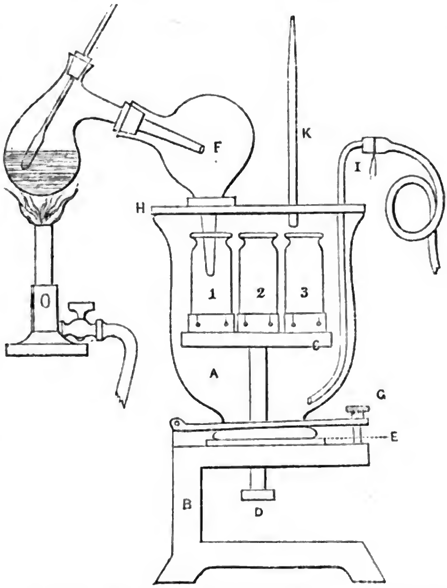
$Sb\,Me_3$		$Sb\,Me_4$		$Sb\,Me_5$	
Sb	74·25	Sb	68·37	Sb	63·19
C_6	20·69	C_8	25·39	C_{10}	29·46
H_9	5·16	H_{12}	6·34	H_{15}	7·35
	100·00		100·00		100·00

Notwithstanding the circumstance that the above samples are not spontaneously inflammable (a character pre-eminently shewn by trimethylstibine), the composition of No. 1, seems to indicate its identity with that body. Before being confident with reference to the composition of Nos. 2 and 3, some weight must be given to an observation here made, viz., that in the decomposition of zinc-methyl by a high temperature, instead of gases being eliminated, as is known to be the case with zinc-ethyl, hydro-carbons are produced which burn with a smoky flame. These substances I have not yet been able to examine, but it would appear that the methyl-molecules undergo duplication, and thus give rise to bodies possessing high boiling points.

It is therefore possible, that pentamethylstibine may be resolved by heat into trimethylstibine and such a hydrocarbon. This would account also for the excess in the carbon and hydrogen given by analysis of sample No. 3.

In conclusion, it is thought that a reviewal of these experiments, in both the ethyl and methyl series, will justify the conclusion that the higher stibium organo-radicals exist. A better method for their isolation however, is still a desideratum.

Apparatus for general fractional Distillation in Carbonic Acid Gas.



A. Inverted bell glass with open neck.

B. Stand with thick vulcanized indian rubber collar E.

C. Circular table with sockets for holding bottles 1, 2, 3, &c.

D. Thick glass rod, sliding air-tight through collar and stand, by which the table and bottles may be raised, lowered, or rotated at pleasure.

F. Quilled receiver and retort.

I. and K. Tubes for entrance and exit of carbonic acid or other gas.

G. Clamp with forked arm, to secure the bell to the stand, and permit the table to rotate eccentrically, if required. The tube of the receiver may thus be introduced into any one of the bottles.

H. Slate cover, which may be ground to fit the lip of the bell, or simply luted to it with linseed.

XIII.—*On Crystallized Sodium and Potassium.*

By Charles Edward Long.

In endeavouring to prepare perfectly bright specimens of sodium and potassium, I have succeeded in obtaining large crystals of both metals. I will briefly describe the method now employed.

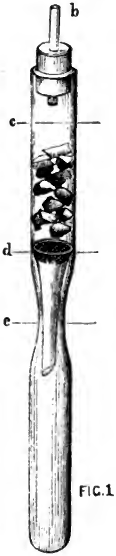


FIG. 1

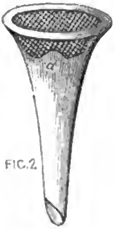


FIG. 2

A piece of the best combustion tube about 2½ feet in length, and ¾-inch in bore, is sealed up at one end, and contracted before the blowpipe at about one-third of its length from the sealed end (fig. 1). A glass funnel with a wide rim (fig. 2) is then prepared so as to fit into the tube as represented, care being taken that the funnel fits *at the rim alone.* Into the filter is introduced a piece of wire gauze, in which a small hole has been cut at *a* (fig 2). The sodium (or potassium) is now introduced into the upper part of the tube in fragments which have been freed from all adhering oxide, and especially from rock-oil, by cutting the metal clean with a knife. Before introducing the metal, the tube is filled with coal-gas which has been dried and partly purified by passing through oil of vitriol. For this purpose, the delivery tube is passed through the tube *b*, which is fitted with a cork into the larger tube.

After the introduction of the metal, the gas is still passed into the tube; the delivery tube is then drawn out and the tube *b* is lightly corked. The large tube is now drawn out and sealed before the blowpipe at *c*, care being taken to avoid melting the metal, lest it should attack the glass and render it brittle. The metal is next fused in the upper part of the tube, and partially poured off from the oxide, so as to present a bright surface for the absorption of any oxygen there may be in the tube. The whole is then allowed to stand for several days, after which the metal is again melted, poured through the filter into the lower portion of the tube, and allowed to solidify. The tube is now cautiously heated at *d*, so as to detach the rim of the filter, which will then readily fall back to the top of the tube on reversing its position, leaving a perfectly clean surface of tube of about 3 inches. The lower tube may now be drawn out and sealed at *e*.

In this manner either metal may be obtained without the slightest tarnish or oxidation. In order to crystallise the metal, it is fused over a Bunsen's lamp, and allowed to cool; as soon as the solid points of crystals appear on the surface, the liquid portion is poured off by suddenly inclining the tube. Specimens prepared in this manner 18 months ago, still retain their lustre unimpaired.

Sodium.—Sodium presenting a perfectly clean metallic surface, is not silver-white, but is of a most beautiful rose colour. The colour is best seen when a ray of light falling upon a surface of the metal is reflected back from a second surface of sodium, and again reflected from the first, so that more of the light of the primitive ray is decomposed than by direct reflection, since the great number of undecomposed reflected rays entirely masks the small number of pink rays, as is the case with silver, which is really yellow and not white. The pink colour of sodium is brought out more strongly by contrasting the metal with bright potassium, which has a greenish-blue tinge.

Sodium is obtained in large octahedra by crystallisation. It does not crystallise in the regular system, but most probably in the quadratic system. As it is impossible to measure the crystals by reflection, owing partly to their being enclosed in a glass tube, but chiefly to the irregularity of the faces which are always striated in a direction at right angles to the major axis, I was only able to measure the facial angles by using a narrow tube provided with an arc, and across which a fine hair was stretched. Unfortunately I have not obtained any crystals with the base-angles well defined. The following are measurements of the angle of the apex:—

		Angle of apex.		
		1	2	3
Crystal I.	face *a* . .	49°·8	50°·0	50°·5
	face *b* . .	50°·5	50°·0	49°·5
Crystal II.	. . .	49°·5	50°·0	49°·5

Potassium.—Has a greenish or greenish blue tint. The beautiful green colour of the vapour may be observed by volatilizing a small portion of the metal in a sealed tube containing no oxygen. It is much more crystalline metal than sodium, but is more difficult to obtain in good crystals, since it passes almost immediately from the liquid to a pasty state. The crystals present an almost smooth metallic appearance for a few moments after the liquid metal has been poured off. Suddenly they assume the appearance of frosted silver, a network of minute lines darting out in every direction. For this reason, they disperse light much more than sodium crystals, whereby the real colour of the metal is effectually masked.

Potassium crystallises in obtuse octahedra belonging to the quadratic system. The following are the measurements of the three facial angles of one of the crystals. In crystal II, I was only able to measure one of the angles of the base:—

			1	2	3
Crystal I.	Angles of base	α	52°·0	52°·0	52°·0
		β	52°·0	52°·0	52°·0
	Angle of apex	γ	75°·5	75°·8	76°·0

		1	2	3	4
Crystal II.	Angle of base	52°·0	51°·5	51°·8	51°·8

XIV.—*On Zinc-methyl.**

By J. A. Wanklyn, F.R.S.E.,

DEMONSTRATOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

Zinc-methyl was discovered rather more than ten years ago by Frankland. It was then obtained nearly pure, but in quantity so small, that many of its leading physical properties, including its vapour-density, specific gravity, and boiling point, were not determined. More recently, the subject has again been taken up by the same chemist, who this time operated upon several pounds of materials, and under conditions widely differing from those of his former experiments.

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* An abstract of this paper was read before the Royal Society of Edinburgh, April 2nd, 1860.

The latter investigation has, however, not been so successful as the former, inasmuch as it has given no pure zinc-methyl, having instead disclosed peculiar and unlooked-for difficulties in the preparation of that compound.

When zinc and iodide of methyl are heated together in closed tubes, the following reactions take place:—

$$(1) \quad . \quad . \quad Zn_2 + C_2H_3I = ZnI.ZnC_2H_3$$
$$(2) \quad . \quad . \quad Zn_2 + 2C_2H_3I = 2ZnI + C_2H_3.C_2H_3.$$

At moderate temperatures, the former reaction predominates; at higher temperatures, the latter. When only iodide of methyl and zinc are employed, and no ether is used, it is impossible to obtain complete decomposition of the iodide without at the same time obtaining much gas. This circumstance renders it impracticable to prepare much zinc-methyl by this method, as the high pressure of the generated gas necessitates the employment of very small tubes. The copper digester, which Frankland employs for the manufacture of this class of substances cannot be made to replace the small glass tubes. Frankland has found that when the materials are heated in the copper digester, no pure zinc-methyl can be obtained.

A mixture of ether with iodide of methyl is easily converted into iodide of zinc and ethereal solution of zinc-methyl. Here, however, a fresh difficulty arises. Fractional distillation does not avail to separate ether from zinc-methyl. And so pertinaciously do these two liquids cling to one another, that it is even a matter of doubt, whether a chemical compound does not exist between them.

To this point our knowledge was advanced by the publication of Frankland's paper* last year.

My attention was drawn to this subject, in the course of my investigation of the compounds formed by methyl with the alkali-metals. These compounds are prepared by acting upon zinc-methyl with the alkali-metals. At first I employed the solution of zinc-methyl in ether, but I found the ether to be a very troublesome complication, and therefore was led to enquire whether it were really impossible to obtain zinc-methyl in a state of purity and at the same time in considerable quantity.

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*Ann. Ch. Pharm. cxi., 62; also Bakerian Lecture, 1859.

During my experiments, I observed the fact that a strong ethereal solution of zinc-methyl, equally with ether, renders the decomposition of iodide of methyl by zinc easy and comparatively unaccompanied by the evolution of free methyl. Thereupon I tried a stronger solution of zinc-methyl and found it also effectual. A still stronger solution was also successful, and it seemed that even pure zinc-methyl itself possessed the same property. Here, then, was an available method of making pure zinc-methyl. Strong ethereal solution of that compound was first prepared. The strong ethereal solution was next mixed with iodide of methyl and sealed up with zinc; then, after digestion in the water-bath, distilled. In this manner, a stronger solution of zinc-methyl was prepared. By repeating the process, a sufficient number of times, the amount of ether originally taken was made to bear a very trifling ratio to the ultimate product; and indeed could be made to vanish altogether.

In evidence of the practicability of the plan just proposed, I may mention, that the product from a single tube, which had undergone four successive digestions, amounted to about half an ounce, and proved to be zinc-methyl as pure as the gramme or two obtained by Frankland ten years ago.

Before giving the analysis of this sample, I will just mention a few particulars connected with its preparation, which may be interesting to any one who may desire to prepare the compound.

The digestions were all made in the water-bath, the substance being always contained in glass tubes. In order that an ounce or two of iodide of methyl might be, with safety, heated in a single tube, the precaution was taken of opening the tube several times in the course of the digestion. By this means, a dangerous accumulation of hydro-carbon gas was avoided. The distillation, of the zinc-methyl was made over the naked flame. Finally, previously to the last distillation, a digestion with metallic-zinc, without any fresh iodide of methyl, was made.

I may also mention that iodide of zinc forms with zinc-methyl, a crystalline compound of great beauty and very different in appearance from the crystalline compound between iodide of zinc and zinc-ethyl. This compound, containing probably one equivalent of zinc-methyl combined with one equivalent of iodide of zinc, I regard as the representative of the so-called iodide of mercury-methyl obtained by Frankland.

Double zinc compound.	Double mercury compound.
$Zn_2 \begin{cases} C_2H_3 \\ I \end{cases}$	$Hg_2 \begin{cases} C_2H_3 \\ I \end{cases}$

Passing on to the properties of the half-ounce of zinc-methyl, whose preparation I have just described:—It was highly inflammable and acted upon water with explosive violence, agreeing with Frankland's description of that compound. In one particular, however, our observations do not accord with one another. The poisonous nature of the fumes, their action upon the nervous system, which Frankland mentions,* I have not been able to verify. I have distilled zinc-methyl more than a dozen times, and been much exposed to its fumes, and still have not been able to mark any particular effect upon myself.

In addition to the properties detailed by Frankland, I have to record that zinc-methyl in a state of purity, is very permanent. If carefully excluded from the atmosphere, it will bear without decomposition a temperature of at least 200° C.

At about 270° C. it begins to be reduced to metallic zinc and hydro-carbon gases.

I have made an analysis of the sample of zinc-methyl with the following results:—

I. ·1134 grm. of the liquid were passed up into a graduated tube standing in the pneumatic trough and filled with water. Hydride of methyl was evolved, measuring 48·77 cubic-centimeters (dry) at 760 m.m. pressure and 0° C. This equals ·034898 grm. by weight:—

Hydride of methyl per cent.=30·77.

II. ·1172 grm. similarly treated gave ·0361 grm. of hydride of methyl or 30·83 per cent.

The theoretical percentage of hydride of methyl, which pure zinc-methyl should give on treatment with water equals 33·51.

These results do not depart from the theoretical quantity further than that which Frankland published ten years ago. His percentage of hydride of methyl was 29·91.

In estimating the value of these determinations, it should be borne in mind that the quantity of hydride of methyl obtained represents its equivalent of unoxidized zinc-methyl. The slightest oxidation tells enormously upon the analysis; for not only does the oxygen lower the percentage of methyl by its presence, but by combining with a certain amount of zinc-methyl, it still further lowers the percentage of methyl which can decompose water.

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* Ann. Ch. Pharm. lxxi., page 214.

The great violence of the reaction between zinc-methyl and water is also a source of loss, especially when water and not mercury is the confining fluid, as was the case in both Frankland's analysis and my own.

A determination of the vapour-density by Gay Lussac's method was also made. ·1163 grm. of zinc-methyl were employed. The temperature to which the vapour was exposed was 100° C; the boiling point of the compound lying between 50° C and 60° C. The experiment gave 3·291 as the vapour density of zinc-methyl. If, as seems likely, the condensation of this compound is analogous to that of its ethyl representative, the theoretical vapour-density is 3·299, a number which is nearly identical with that found by experiment.

The accurate determination of its boiling point, and also of the specific gravity in the liquid state, I hope shortly to have an opportunity of making, as I expect at no very distant period to be in possession of several ounces of pure zinc-methyl.

I cannot conclude this paper without calling attention to the very remarkable state of condensation, disclosed by examination of the vapour-densities of zinc-ethyl, zinc-methyl, mercury-ethyl, mercury-methyl, and indeed of all the so-called organo-metallic bodies so far as has yet been investigated.

It has been said, the metals are the strict representatives of hydrogen; and yet, in not a single compound of a metal with a hydro-carbon radical, has the metal been found in the state of condensation of hydrogen. If we write the formulæ of equal volumes of several of these bodies, we arrive at the following expressions:—

Zinc-methyl. Zinc-ethyl. Mercury-methyl Mercury-ethyl

$$\left.\begin{array}{l}C_2H_3\\C_2H_3\end{array}\right\}Zn_2; \quad \left.\begin{array}{l}C_4H_5\\C_4H_5\end{array}\right\}Zn_2; \quad \left.\begin{array}{l}C_2H_3\\C_2H_3\end{array}\right\}Hg_2; \quad \left.\begin{array}{l}C_4H_5\\C_4H_5\end{array}\right\}Hg_2;$$

Distann-methyl. Distann-ethyl.

$$\left.\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{array}\right\}Sn_2; \quad \left.\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{array}\right\}Sn_2.$$

Writing also the formulæ of equal volumes of the hydrogen and oxygen terms for comparison with the former:—

Hydride of methyl.	Hydride of ethyl.	Methyl-ether.	Ethyl-ether.
$\left.\begin{matrix}C_2H_2\\H\end{matrix}\right\}$;	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\} O_2$	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\} O_2$.

Inspection of the above shows that, considered as to the state of condensation in their hydro-carbon compounds, the metals do not represent hydrogen: mercury and zinc represent oxygen.

Nor is this peculiarity confined to the organic case. Deville and others have recently taken the vapour-density of various metallic chlorides and have found that these likewise are present in a more condensed form than their hydrogen representative. Whereas the formula of hydrochloric acid is $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, the formula of an equal volume of metallic chloride is $\left.\begin{matrix}M_2\\Cl_2\end{matrix}\right\}$ or $\left.\begin{matrix}M_4\\Cl_6\end{matrix}\right\}$ &c.

XV.—*On some derivatives from the Olefines.*

By Frederick Guthrie.

III.

The introduction of nitroxine* into organic bodies, and the formation of the so-called nitro-compounds, has been hitherto effected, with apparently a single exception† by the action of nitric acid, either alone or in presence of sulphuric acid. The reason of this is obvious:—such introduction has, in every case, consisted in the *replacement* of hydrogen by nitroxine. The nitric acid offers its fifth atom of oxygen to the hydrogen being replaced, while, the nitroxine replaces it. Such replacement is of course double recomposition expresssed generally by the equation,

$$C_m \ldots H_n + p(ONO_4) = C_m \ldots H_{n-p}(NO_4) + pHO$$

and is quite parallel to the reaction attending the formation of

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*It will be found convenient to call NO_4 *nitroxine*, a compact term, recalling the analogy which this molecule bears to chlorine, iodine, etc.: Accordingly the nitrites, $MONO_2$, will be nitroxides MNO_4 as has been sometimes proposed.

Further regarding the nomenclature, as with the chlorides, $C_4H_2Cl_2$ is bichlorethylene, $C_4H_4Cl_2$ bichloride of ethylene, etc.:—So with the nitroxides:

$C_{20}H_7NO_4$, Nitroxinapthaline

$_{10}H_{12}2NO_4$. Binitroxide of Amylene, etc.

† See below; nitroxinapthaline.

the chlorine substitution derivatives obtained by the action of chlorine,

$$C_m \ldots H_n + p(Cl\ Cl) = C_m \ldots H_{n-p}Cl + pHCl$$

and probably also to that which occurs when chlorine is introduced by means of hypochlorous acid.

The formation of binitroxide of amylene, $C_{10}H_{10}.2NO_4$, by the action of nitric acid upon amylene,* immediately suggested the question:—May the olefines whose privilege it is to combine directly with two atoms of the halogens, without elimination of hydracids, behave in a similar manner towards nitroxine?

If nitroxine, prepared by heating anhydrous nitrate of lead, be passed through an empty bottle and then into a flask containing amylene, the gas is instantly absorbed and the amylene gradually becomes converted into a pasty mass of minute crystals. To avoid loss, the flask containing the amylene should be surrounded by a freezing mixture. The product is thrown upon a filter, washed with cold alcohol in order to remove an oily liquid which accompanies the crystals, then recrystallised from boiling ether, and dried in *vacuo* over sulphuric acid.

.I. 0·2682 grm. gave 0·3664 grm. carbonic acid and 0·1572 water.

II. 0·2290 grm. gave 32·3 cc. of nitrogen at 760 mm. and 0° C which gives,

	Calculated	Found	
		I.	II.
C_{10} . .	37.09	37·26	,,
H_{10} . .	6·18	6·51	,,
N_2 . .	17·28	,,	17·66
O_8 . .	,,	,,	,,

This substance is therefore the binitroxide of amylene $C_{10}H_{10}.2NO_4$ and is identical with the crystalline body obtained by the action of nitric acid upon amylene (see II). It is curious as being the only known nitroxine-isotype of Dutch liquid, but more remarkable, in this latter manner of its formation, as furnishing the only instance in organic chemistry of the behaviour of free nitroxine as a halogen without the elimination of hydrogen. Bintroxide of amylene is but slightly soluble in cold, but readily in boiling alcohol; it dissolves in ether and in bisulphide of carbon but is perfectly insoluble in water. It crystallises in small square and rectangular, colourless, transparent plates.

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*See II.

Heated by itself in a dry tube, binitroxide of amylene decomposes exactly at 95° C., giving rise to a gas and to a liquid heavier than water. The decomposition of a portion having been effected in a very strong sealed tube by heating to 100° C., the tube on opening gave off much gas, which reddened moist litmus paper. Another portion was treated in the same way in presence of water. After opening the tube, neutralizing the acid water with ammonia, filtering, and evaporating to dryness on a water bath, a residue was obtained, which gave off nitrogen on being heated. Accordingly, the gas evolved from the binitroxide of amylene was nitrous acid, NO_3, or nitroxhydric acid HNO_4.

The next point was to determine the nature of the liquid product, the supplementary factor to binitroxide of amylene, which appears in the preparation of that body.

The filtrate and alcoholic washings from binitroxide of amylene, after evaporation for some hours on a water bath, washing with water and drying, yielded an amber-coloured transparent liquid, heavier than water and immiscible with it.

Neither this liquid nor the binitroxide of amylene underwent any change on being kept for several days in an atmosphere of nitroxine.

On analysing the liquid:

0·2586 grm. gave 0·3882 grm. of carbonic acid and 0·1717 water.

The substance whose composition corresponds most closely with these numbers, is a mixture of equivalent quantities of binitroxide of amylene with nitrate of amyl.

	$C_{10}H_{10}.2NO_4$ $C_{10}H_{11}O.NO_5$	Found.
C . .	40.67	40·94
H . .	7.12	7·37

Although the presence of amyl would point to the disintegration of another molecule of amylene, the above given composition of this mixture is rendered probable on the following grounds:—On heating to 95° C.,* it undergoes decomposition, whereupon the temperature rises spontaneously to 170° C., and the greater quantity of the liquid passes over. On rectifying, a portion was obtained which boiled almost constantly at 160° C. Of this,

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* Identical with that at which $C_{10}H_{10}.2NO_4$ is decomposed

0·2263 grm. gave 0·3850 grm. carbonic acid and 0·1712 grm.

	$C_{10}H_{11}ONO_5$	Found.
C . .	45·11	46·40
H . .	8.27	8.40

On boiling a portion of this distillate with an alcoholic solution of caustic potash, nitrate of potash was formed. The original liquid also gave rise to nitrate of potash under the same circumstances.

Nitrate of amyl also appears among the liquid products formed when binitroxide of amylene is heated by itself.

Heated with quick lime, binitroxide of amylene gives rise to an aromatic body, differing from valeral and probable amylenic ether $C_{10}H_{10}O_2$.

The actions of sulphide of ammonium, nascent hydrogen, and other reducers, upon binitroxide of amylene, will be well worthy of study.

As yet, my attempts to combine nitroxine with ethylene have not been successful.

Neither protoxide nor binoxide of nitrogen has any action upon amylene. The affinity of amylene for nitroxine is so great that by means of this hydrocarbon, a very small trace of nitroxine may be detected in the above named nitrogen-oxides. Thus if amylene be added through a funnel tube to a flask containing copper and nitric acid which is kept quite cold and from which the evolved gas has expelled the air, crystals of binitroxide of amylene are continuously though slowly formed; but if the binoxide of nitrogen be first absorbed by protosulphate of iron and then expelled thence by heat* and made to pass through amylene in an apparatus from which a current of carbonic acid has expelled the air, no change occurs.

Nitroxinapthalin. (Nitronapthalin.)

The laborious reseaches of Laurent† and others have long since established the claim of napthalin to be an olefine. It combines directly with chlorine to form bichloride of napthalin $C_{20}H_8Cl_2$, and although it may unite with four atoms of halogen as in the quadrichloride $C_{20}H_8Cl_4$, in the terchloro bromide $C_{20}H_8Cl_3Br$, and in their numerous idiotypes,

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* Bunsen's Gasometry. Engl. Ed. p. 51.

† Ann. Ch. Phys., 1835, lix.

$C_{20}H_6Cl_2Cl_4$ quadrichloride of bichlornapthalin.
$C_{20}H_6Br_2Cl_4$ quadrichloride of bibronapthalin,
etc. etc.

yet, as we have already seen in examining the behaviour of ethylene and amylene towards chloride of sulphur, and as we shall abundantly see in the sequel, this assumption of four haloid atoms is quite consistent with the nature of the olefines isotypic with ethylene. Like ethylene, napthalin combines with anhydrous as well as with hydrated sulphuric acid, and finally in napthalamine $C_{20}H_8HN$ we find it still preserving the biatomic character of an olefine, taking the place of two atoms of hydrogen.

Laurent's examination of the action of nitric acid on napthaline resulted principally in the discovery of three nitroxine-replacement derivatives, idiotypic not with the bichloride of napthalin, but with napthalin itself.

Nitroxinapthalin . . .	$C_{20}H_7(NO_4)$
Binitroxinapthalin . .	$C_{20}H_6(NO_4)_2$
Trinitroxinapthalin . .	$C_{20}H_5(NO_4)_3$

Bearing in mind, on the one hand, the analogy which these bodies have to the chlorine-idiotypes of ethylene, and on the other, the above described direct union of amylene with nitroxine, we might *à priori* expect to obtain nitroxide of napthalin or binitroxide of napthalin by the action of nitroxine on napthalin. So that, although Laurent gives this reaction as a method of preparing nitroxinapthalin, yet, as no analysis appears to have been made of the body so produced, I thought it worth while to comfirm Laurent's experiment.

If napthalin be thrown into a flask containing an excess of nitroxine, considerable heat is developed, scanty white fumes are formed, which quickly subside, and an oily liquid results which solidifies on cooling. To ensure complete reaction, the flask is corked with an excess of nitroxine, and the product is repeatedly shaken and melted. After re-fusion under water, drying, and recrystallisation from ether, a product was obtained which gave on analysis

0·4202 grm. gave 1·0707 grm. CO_2 and 0·1590 grm. water.

	$C_{20}H_7(NO_4)$	Found.
C . .	69·36	69·49
H . .	4·05	4·20

The substance formed is therefore undoubtedly nitroxinapthalin. We accordingly find that nitroxine, in its behaviour towards napthalin, more closely resembles bromine than chlorine; for while the former gives bromonapthalin, the latter gives bichloride of napthalin,

$$\begin{aligned} C_{20}H_8 + 2Cl &= C_{20}H_8Cl_2 \\ C_{20}H_8 + 2Br &= C_{20}H_7Br + HBr \\ C_{20}H_8 + 2NO_4 &= C_{20}H_7NO_4 + HNO_4, \end{aligned}$$

Bisulphochloride of Ethylene.

Although, as before shown,* ethylene and bisulphide of chlorine are without appreciable action on one another under ordinary circumstances of temperature, etc., and although a temperature of 139° C., effects a disintegration of the ethylene-molecule†.

I have again sought to unite the two directly, because the resulting body, if it resemble its amylene-isotype, would give rise to a highly important series of derivatives.‡ If bichloride of sulphur be exposed in a stoppered bottle in an atmosphere of dry ethylene to direct sunlight, the two unite slowly but almost completely, hydrochloric acid however being liberated.

If a few grammes of bisulphide of chlorine be placed in a well-stoppered bottle which is then filled by displacement with ethylene, the waxed stopper inserted and covered with sheet-caoutchouc, and the whole be completely immersed for twenty hours in boiling water, very complete absorption is found to have taken place on opening the bottle, while only a trace of hydrochloric acid is formed. The bottle may be then refilled with ethylene and the same operation repeated three or four times. The resulting product is then shaken up with warm water, dried, digested with ether, filtered, evaporated *in vacuo* till the ether is expelled, dissolved again in a minimum of ether filtered, and evaporated *in vacuo*.

	grm.		grm.		grm.	
I.	0·3058	gave	0·2908	carbonic-acid and	0·1184	water.
II.	0·2197	„	0·2356	water.		
III.	0·1798	„	0·2638	chloride of silver.		
IV.	0·2829	„	0·6934	sulphate of baryta.		

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* Niemann. Ann. Ch. Pharm. cxiii. 3; F. Guthrie, *ibid.*

† Chem. Soc. Qu. J. March, 1860.

‡ See Memoir iv.

	Found.				
$C_4H_4S_2Cl$	I.	II.	III.	IV.	
C = 25·13	25·93	”	”	”	
H = 4·19	4·30	(4·33)	”	”	
S = 33·51	”	”	”	33·47	
Cl = 37·17	”	”	36·29	”	
100·00					100·01

This substance is, according to the previously adopted nomenclature, the *bisulphochloride of ethylene*, $C_4H_4.S_2Cl$.

Bisulphochloride of ethylene has a not unpleasant but indescribable smell; its taste is intensely sweet and pungent. Like the bichlorosulphide of ethylene, its annoying effect upon the eyelids is very enduring;* Its colour is a pale yellow; specific gravity 1·346 at 19 C.° Like the previously described chlor-sulphur compounds of the olefines, it is decomposed by heat and gives off an insupportable smell.

In the next communication, I shall describe the action of anhydrous and hydrated oxides upon this substance, and the behaviour of it and its isotype, bisulphochloride of amylene, upon some of the metal-radicles.

XVI.—*Contribution towards the history of Cinnamic Acid.*

By David Howard.

Notwithstanding the experiments of Gerhardt and Cahours, and the subsequent researches of Blyth and Hofmann, the history of cinnamol and its derivatives is far from being complete. To fill up some of the gaps still existing, I engaged in some experiments upon this interesting group of substances. In the prosecution of my enquiry, I had an opportunity of observing some facts, which I beg to lay before the Chemical Society.

Liquid storax treated in the usual way afforded the crude cinnamic acid for the experiments. For the purpose of purifying it, I adopted the plan recommended by some chemists, of submitting the crude product to careful distillation. To my surprise, a large portion of the distillate came over in the form of a permanent liquid. The smaller portion, which solidified on cooling, was purified by crystallisation and converted into a silver salt. The silver determination gave the following result:

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* A drop placed beneath the tongue destroys the epidermis and causes a soreness which lasts many days.

·2090 grm. of the silver-salt left on ignition
·09850 grm. = 47·13 per cent of metallic silver.

The percentage of silver in benzoate of silver being 47·16, it was obvious that the solid distillate consisted of benzoic instead of cinnamic acid. To find whether this benzoic acid was present in the original crude acid, or whether it had been formed by the destruction of cinnamic acid, a portion of the crude acid was recrystallized and converted into a silver-salt.

·5735 grm. of this salt left on ignition
·2500 grm. of metallic silver = 43·59 per cent.

42·37 being the percentage of silver in cinnamate of silver, it could not be doubted that the crude acid employed contained an appreciable admixture of benzoic acid. It was therefore further purified by solution in alcohol and crystallisation by spontaneous evaporation of the solvent, when large regular crystals were obtained, which, on analysis of a new silver-salt, proved to be pure cinnamic acid.

·5170 grm. left ·2190 = 42·36 per cent. of silver
·5085 grm. left ·2150 = 42·28 per cent. of silver.

These numbers coincide with the theoretical percentage of cinnamate of silver.

A careful distillation of this pure acid, afforded, together with a large portion of an oily product, a small quantity of an acid which solidified in the neck of the retort. This acid was converted into a silver-salt and in this form submitted to analysis:—

·2255 grm. left on ignition ·0955 = 42·35 per cent. of silver,
·2165 grm. left on ignition ·0915 = 42·27 per cent. of silver.

The distilled acid was therefore undecomposed cinnamic acid. In other experiments in which the acid was submitted to a still slower distillation, the whole of it was entirely decomposed and converted into liquid products of decomposition.

Thus it would appear that cinnamic acid, contrary to the statements of most Manuals, is decomposed when kept at a boiling heat, and that it can only be distilled even partially unchanged, when very rapidly heated, care being taken to carry over the vapour as quickly as possible by keeping the upper part of the retort at a very high temperature.

In order to find whether cinnamic acid would decompose when maintained for a long period at a somewhat lower temperature, a portion of the acid was sealed up in a glass tube, and heated for several hours to 200° C. in a paraffin bath; no change however took place.

Another portion was similarly heated in presence of water. It remained likewise unchanged, the silver-salt yielding the following percentage:—

·4805 grm. gave ·2040 = 42·45 per cent. of silver.

The fluid which is formed by the action of heat upon cinnamic acid, proved on investigation to be almost pure cinnamol; the boiling point remained constant at 145° C., till the greater part of the liquid had passed over, when the temperature rose rapidly, leaving in the retort a resinoïd mass of *metacinnamol.* By treating the liquid with bromine the characteristic crystalline dibromide of cinnamol was obtained; and by exposing a portion sealed up in a tube to 200°, it was entirely converted into a glassy mass of metacinnamol, which when submitted to a still higher temperature, was reconverted into cinnamol.

These properties identify the oily product of decomposition of cinnamic acid with cinnamol, or what is the same thing, with styrol, although it appears that the tendency to pass into the solid condition is perhaps less marked in this liquid than in styrol, a fact noticed by other observers in cinnamol formed by the usual process. When very carefully heated, cinnamol obtained by the destructive distillation of cinnamlic acid may be almost entirely distilled without the production of the solid modification.

The preceding experiments prove that at a temperature very near its boiling point, cinnamic acid is decomposed into cinnamol and carbonic acid, according to the equation,

$$C_{18}H_8O_4 = C_{16}H_8 + 2CO_2,$$

a decomposition similar to the transformation into benzol and carbonic acid, which benzoic acid undergoes when its vapour is passed through a red hot tube.

The cinnamol thus obtained from cinnamic acid amounts to from a fourth to a third of the acid employed, so that this reaction furnishes a method of preparing cinnamol much more easily and much more copiously than it could be hitherto obtained. Cinnamol obtained in this manner is perfectly free from benzol. It is well known that the liquid obtained by the usual process viz., distillation of cinnamic acid with lime and even baryta, consists of a mixture of hydrocarbons, in which so large a proportion of benzol is present, that some chemical Manuals state the boiling point of cinnamol at 89° C., proving that the proportion of cinnamol in these mixtures is excessively small. The dry distillation of pure cinnamate of lime likewise furnishes cinnamol quite free from benzol, thus affording a remarkable contrast to the behaviour of a mixture of cinnamic acid and excess of lime.

The crude cinnamol obtained from either cinnamic acid or cinnamate of lime, contains a small quantity of a crystalline substance which may be separated from the more volatile cinnamol by distillation with water; the formation of metacinnamol is thus in a great measure prevented, and the substance in question may be extracted from what is left in the retort by alcohol, from which it crystallises. When purified by several crystallisations from boiling alcohol, which dissolves it freely, while cold alcohol retains a comparatively small portion, the crystalline substance presents itself in the form of brilliant pearly scales which on analysis gave the following results:—

I. ·1563 grm. gave ·5341 carbonic acid and ·0992 water.
II. ·2500 grm. gave ·8605 carbonic acid and ·1545 water.

These numbers represent a hydrocarbon $C_{14}H_6$ or a multiple of it,

	Theory		Experiment	
			I.	II.
C_{14}	84	93·33	93·19	93·76
H_6	6	6·67	7·05	6·86
	90	100·00		

The crystalline substance when gently heated with bromine, gives rise to the formation of a bromine-compound which is only slightly soluble even in boiling alcohol. The hot solution deposits on cooling, minute scales exhibiting a slightly reddish tint. On analysis the following results were obtained:—

I. ·2780 grm. gave ·5060 carbonic acid 0·985 water,
II. ·1915 grm. gave ·2120 bromide of silver,
III. ·2020 grm. gave ·2255 bromide of silver.

The formula $C_{14}H_6Br$ requires the following values which I place in juxtaposition with the experimental numbers:—

	Theory		Experiment		
			I	II.	III.
C_{14}	84	49·41	49·64	——	——
H_6	6	3.53	3.68	——	——
Br	80	47·06	——	47·10	47·50
	170	100·00			

The formation and composition of the bromine-compounds could leave but little doubt that the crystalline hydrocarbon must be represented by the formula $C_{28}H_{12}$.

A hydrocarbon of precisely the same composition, and exhibiting also the general characters of the substance derived from cinnamic acid, was described some years ago by Laurent. He obtained the body which he calls "stilbene," together with another crystalline body, "thionessal," in the destructive distillation of hydride of sulphobenzoïl thus,

$$\underset{\text{Hydride of Sulphobenzoïl}}{8\,C_{14}H_6S_2} = 2C_2S_4 + 6HS + \underset{\text{Stilbene}}{2C_{28}H_{12}} + \underset{\text{Thionessal}}{C_{52}H_{18}S_2}.$$

In order to establish the identity of the two substances, I have prepared a quantity of stilbene, according to Laurent's process In repeating the experiments of Laurent, I observed all the phenomena described by that chemist.

On comparing the stilbene procured in this manner with the crystalline substance obtained from cinnamic acid, it was impossible to doubt their absolute identity. I have nothing to add to Laurent's description, except that stilbene prepared by the dry distillation of either hydride of sulphobenzoïl, or of cinnamic acid, fuses at 125° C.

The transformation of cinnamic acid into stilbene is obviously the result of a destructive process, which does not admit of simple representation in formulæ.

The experiments which I have described were performed in Dr. Hofmann's laboratory.

XVII.—*Action of Sodium upon Iodide of Methyl mixed with Ether.*

By J. A. Wanklyn, F.R.S.E., and F. Buckeisen, Ph.D.

Pure methyl has not yet been obtained. Kolbe's method, viz., electrolysis of an acetate, yields methyl always contaminated by some foreign body, probably oxide of methyl, which cannot be completely removed.

Frankland's method, viz., decomposition of iodide of methyl by zinc, also gives a mixture, which, in this case, consists of hydride of methyl and free methyl. This hydride of methyl, Frankland regards as a secondary product, formed after the gas has left the production tube, and due to decomposition of moisture by some zinc-methyl, with which the gas, as it issues forth, is invariably accompanied.

Bearing this circumstance in mind, we determined to try the action of sodium upon iodide of methyl. Since sodium-methyl cannot be prepared by such a process, we expected to obtain pure methyl. Our expectation was not realized, as will appear in the course of the paper.

The iodide of methyl used in our experiments, boiled constantly at 43° C.

We enclosed in a glass tube some sodium along with a few grammes of iodide of methyl and ether. In order to insure the absence of moisture, we next made a short preliminary digestion in the water-bath. Then we let out the first portion of gas, which was no doubt contaminated with products due to traces of water adhering to the materials employed in the experiment. Afterwards we resealed the tube, heated again to 100° C., and collected the gas over boiling water. After having stood in contact with water during a night, the gas was analysed according to the method employed by Bunsen.

We give the particulars of the analyses:—

The gas was divided into two portions, one of which was placed in the combustion eudiometer, and the other in the absorption tube.

I.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume of gas taken	72·00	26·9°C.	meter 0·15085	9·8876
Volume after addition of oxygen ..	180·96	27·1°	0·25844	42·547
Volume after addition of air	340·90	26·2°	0·41561	129·28
Volume after explosion	308·54	26·7°	0·38336	107·74
Volume after absorption of CO_2 ..	275·42	25·5°	0·378	95·221
Volume after addition of Hydrogen ..	375·0	26·7°	0·4717	161·13
Volume after explosion	252·98	27·3°	0·3575	82·23

II.—*In the absorption tube.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume of gas taken	93·70	26·9°	meter 0·65305	55·706
Volume after the action of potash and pyrogallic acid	90·63	26·6°	0·6781	55·591
Volume after the absorption of olefines	82·8	25·5°	0·6675	50·551

Some gas after the removal of CO_2, oxygen and olefines, was transferred from the absorption tube to the eudiometer. Its analysis gave the numbers following:—

III.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume taken	84·32	26·7°C.	meter 0·16676	12·609
Volume after the addition of oxygen	399·36	26·7°	0·48686	177·12
Volume after explosion	364·95	27·8°	0·45242	150·11
Volume after the absorption of carbonic acid	330·25	25·1°	0·4463	134·99

Another analysis of the same gas yielded:—

IV.—*In the Eudiometer.*

Corrected at 0° C. and one meter pressure	
Volume taken	10·365
Volume after the addition of oxygen	160·75
Volume after explosion	138·40
Volume after absorption of CO_2	125·60

A third analysis of the same gas gave:—

V.—*In the Eudiometer.*

Corrected at 0° C. and one meter pressure	
Volume taken	18·037
Volume after the addition of oxygen	85·611
Volume after the addition of air	198·04
Volume after explosion and absorption of CO_2	137·05
Volume after addition of hydrogen	258·67
Volume after explosion	114·73

Analysis II. shows that the gas was free from carbonic acid and oxygen. It also shows that 55·706 volumes of the gas contained 5·155 vol. of olefines.

In percentage C_nH_n . .	9·3
Gas freed from C_nH_n . .	90·7
	100·0

Analysis I. shows that 9·8876 vols. of gas contain 0·368 vol. of nitrogen. In percentage nitrogen = 3·7.

Analysis V. of the gas free from C_nH_n shows that 18·037 vols. contain 0·21 vol. of nitrogen, or 90·7 vols. contain 1·05 vols. of nitrogen. But 100 vols. of the original gas contain 90·7 vols. of gas free from C_nH_n. Therefore, 100 vols. of the original gas contain 1·05 vols. of nitrogen.

The determination of nitrogen at the end of a hydro-carbon gas analysis is subject to a little irregularity, inasmuch as the small quantities of air introduced in the course of the analysis, tell in the aggregate upon the final nitrogen determination.

Adopting the mean of our two results, we have 2·4 for the percentage of nitrogen.

From Analysis I. we obtain:—

		In percentage.
Original gas . . .	9·8876	100·0
Nitrogen . . .	0·237	2·4
Combustible gas . .	9·6506	97·6
Oxygen consumed . .	24·4084	246·9
Carbonic acid formed .	12·519	126·6

Analyses III., IV., and V., all of the residual gas after removal of C_nH_n give:—

	III.	IV.	V.	Mean.
Combustible gas .	12·507	10·091	17·560	88·3
Oxygen burnt .	29·623	25·059	43·430	215·7
Carbonic acid formed	15·120	12·80	—	109·1

To arrive at the condensation of the olefines we make use of the following data:—

100 vols. of the original gas are composed of,

9·3 vols. of C_nH_n.
2·4 vols. of nitrogen.
88·3 vols. of residual hydro-carbon.

And on combustion furnish,

246·9 vols. oxygen consumed.
126·6 vols. carbonic acid.

88·3 vols. of the residual hydro-carbon gas furnish

215·7 vols. oxygen consumed.
109·1 vols. carbonic acid.

Hence the 9·3 vols. of C_nH_n furnish

31·2 vols. oxygen consumed.
17·5 vols. carbonic acid.

The C_nH_n, therefore, has the condensation of ethylene, which requires,

Vol. taken	1·0
Oxygen burnt	3·0
Carbonic acid	2·0

With so low a percentage of C_nH_n as is present in the gas under examination, great accuracy in the determination of its condensation is not to be expected; the very indirect manner of arriving at the result having the effect of concentrating the errors of the whole analysis upon the small percentage of olefine.

The 88·3 vols. of hydro-carbon must consist, for the most part, of marsh gas. Some other more complex hydro-carbon is also present; but what other, cannot be revealed by a mere combustion analysis. If the hydro-carbon be very complex, then the percentage of marsh gas must be high; if less complex, then the percentage of marsh gas falls.

Assuming that the accompanying hydro-carbon is methyl, in which case the proportion of marsh gas reaches its lowest, we have for the composition of the gas

C_4H_4	9·3
Nitrogen	2·4
Hydride of methyl	65·0
Methyl	23·3
	100·0

As is well known, a combustion cannot distinguish marsh gas from a mixture in equivalent quantities of methyl and hydrogen.

That our marsh gas was such a mixture, was highly improbable. Direct proof we have nevertheless sought in another experiment.

We made a fresh quantity of gas, collected it over strong alcohol (previously boiled) and shook it up therewith. Since methyl is very much more soluble in alcohol than is hydrogen, the gas discharged from this alcohol by boiling, should have been very rich in methyl. After washing with water, however, it yielded on combustion numbers agreeing with the composition of hydride of methyl, viz.:—

Contraction.		Carbonic Acid.
10·31	:	5·27

Hydride of methyl requires contraction to carbonic acid in the ratio of 2 : 1.

This gas also contained hardly any olefine, viz., only 2·7 per cent.

We have thus established the following conclusions:—

At 100° C. sodium decomposes iodide of methyl in presence of dry ether, yielding a large quantity of hydride of methyl.

The equation expressing the production of the hydride is neither of the following:—

$$Na_2 + 2(C_2H_3I) = 2NaI + C_2H_2 + C_2H_4$$
$$Na_4 + 4(C_2H_3I) = 4NaI + C_4H_4 + 2(C_2H_4)$$

because, the amount of C_nH_n is too small for the hydride of methyl.

What the product, complementary to the hydride of methyl, really consists of, we have not yet been able to determine.

In conclusion we have to add that we have repeated the experiment and obtained similar results to those which we have described in the paper. With potassium likewise the sâme peculiarity has been observed as with sodium.

The further investigation of the subject will be made by one of us,

XVIII.—*On the Composition of the Aqueous Acids of constant Boiling Point.*

BY HENRY ENFIELD ROSCOE.

IT is still a very generally received opinion, that a liquid which boils unchanged at a fixed temperature must be regarded as a chemically homogeneous body. This supposition is not, however, borne out either by theoretical considerations or by practical experience.

The proportions in which the constituents of a mixed liquid pass, on boiling, into the state of vapour depend upon the proportions in which the constituents are contained in the liquid, and upon the separate tensions of the vapours of these constituents at the temperature of ebullition. Although the laws which regulate the vaporization of mixed liquids are as yet far from being understood, it is easy to see that the relations between the several tensions and the proportions by weight of the two or more constituents may be such that, at a given temperature of ebullition, the composition of the vapour is identical with that of the liquid. As soon as this point is reached, the mixed liquid boils at a constant temperature without undergoing any change of composition, and in this respect does not differ from a uniform chemical combination. Such mixed liquids possess, however, other properties, by means of which they can be easily distinguished from definite chemica lcombinations. The characteristics by which a chemical compound is recognized, are generally considered to be (1), that the components of such a combination are united in quantities represented by some simple atomic relation; and (2), that this relation remains unaltered under a certain change of physical conditions.

From the experiments of Dalton, Mitscherlich, Millon, Bineau, and others, it has been hitherto supposed that most of the aqueous acids, and especially hydrochloric, hydrobromic, hydriodic, hydro-fluoric, nitric, and sulphuric acids, of very various degrees of strength, not only attain a fixed composition when boiled under the ordinary atmospheric pressure, but that the liquids thus prepared are definite chemical compounds of acid and water. In the present communication, my aim will be to show that this latter supposition is incorrect; that although liquids possessing constant composition are obtained by boiling the above-mentioned acids under the ordinary atmospheric pressure, these bodies cannot be regarded as definite hydrates, but that the phenomenon of constant composition and fixed boiling-point is to be ascribed to the establishment of that particular relation between the weights and tensions of the constituents, by virtue of which acid and water are contained in the vapour in the same proportions in which they are present in the liquid. I shall show, in the first place, that the composition of the acids obtained by ebullition under the ordinary atmospheric pressure, does not, in the case of any of the acids examined, with one exception, agree with that of a simple hydrate; and, secondly, that in every case when these constant acids are brought under other physical conditions, such as when boiled under different pressures, or when a current of dry air is passed through them at different temperatures, they are decomposed and attain a different but constant composition, so that a mixture of acid and water may be made which, on vaporization at a given temperature, does not undergo any alteration in composition.

1. *Nitric Acid.*

Dalton was the first clearly to point out that mixtures of nitric acid and water, when boiled, undergo such a change that the weak mixtures lose water, and the strong mixtures lose acid, until the residual liquid attains a specific gravity of 1·42, and boils, under the ordinary atmospheric pressure, steadily at 120° C. This observation has since been confirmed by the experiments of Mitscherlich, Bineau, Millon, and Smith. The residual acid obtained by boiling either a weaker or a stronger acid was found by these chemists to possess an almost constant composition, the analyses giving an amount of nitric acid (HNO_6) varying from 66 to 70 per cent. on the liquid. From his own experiments Mitscherlich concluded, that this acid of constant boiling point contains 4 atoms of water to 1 atom of HNO_6, whilst Bineau and others supposed that this acid consists of 3 atoms of water and 1 of nitric acid (HNO_6), corresponding to the well-known series of magnesian nitrates of the formula RNO_6+3HO.

Owing to the discrepancy in these statements, it appeared of interest to determine, as accurately as possible, in the first place, whether the acid obtained by distillation under the ordinary atmospheric pressure has a constant composition; and, secondly, whether the relation between acid and water is one capable of expression in simple numbers. For this purpose, a quantity of strong acid was prepared by the usual processes,* and freed completely from lower oxides of nitrogen by passing a current of dry carbonic acid through the warm liquid. The acid thus prepared was perfectly colourless, and free from every trace of chlorine and sulphuric acid. The method of determination adopted, consisted either in volumetric analysis with a standard solution of caustic soda of exactly known strength, or in neutralizing the acid with a weighed quantity of pure fused carbonate of sodium, boiling the solution, and adding a small quantity of test acid or alkali to reach the exact point of neutrality, which was supposed to be attained when the litmus became blue. The quantity of acid employed for each determination was such, that the maximum analytical error, the amount of which was determined by control experiments, never attained 0·2 per cent. on the liquid. In order to check the two methods employed, an acid, which with test alkali was found to contain 68·00 per cent. of HNO_6, and with pure carbonate of sodium gave 68·02 per cent. of HNO_6, was neutralized with freshly precipitated carbonate of barium, the barium in solution being estimated as sulphate; 1·3368 grms. of the nitric acid yielded 1·6815 grms. of sulphate of barium, corresponding to 67·95 per cent. of HNO_6.

The composition which aqueous nitric acid of various degrees of strength attains when boiled under the ordinary atmospheric pressure, was determined by diluting portions of the pure concentrated acid to a given extent with water, and, after analysis, distilling them in a small retort, the strength of the residual liquid being then accurately estimated. The experimental results are contained in the following Table, in which Column I gives the volume of acid employed; Column II, the percentage quantity of real acid (HNO_6) contained in the liquid before distillation; Column III, the volume of liquid remaining in the retort; and Column IV, the percentage quantity of real acid (HNO_6) contained in the residual liquid after distillation.

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* Millon's statement respecting the difficulty of separating from the distillate the sulphuric acid used for concentrating the nitric acid was not confirmed. Strong nitric acid was easily obtained free from every trace of either sulphuric or hydrochloric acid.

TABLE 1.

No.	I.	II.	III.	IV.
(1)	25 cbc.	99·8	5 cbc.	95·8
(2)	25 „	95·2	5 „	84·8
(3)	25 „	84·7	5 „	71·8
(4)	120 „	77·8	20 „	69·1
(5)	180 „	74·7	8 „	68·1
(6)	120 „	70·5	20 „	68·6
(7)	90 „	70·5	15 „	68·6
(8)	120 „	65·1	30 „	68·0
(9)	120 „	65·1	20 „	68·3

From these experiments it is seen, that nitric acids of widely different degrees of concentration attain on boiling a composition varying from 68 to 69 per cent. of real acid. The slight differences in the composition of the residue here observed, arise from the impossibility of performing the experiments under the same physical conditions, as overheating the vapour, unequal exposure to air, &c., cannot be avoided. This is proved by comparing the results of a second series of experiments, detailed in Table 2. The distillation was, in these instances, effected in a small bulb-tube retort, blown before the lamp, in which the ebullition in presence of platinum proceeded more regularly and quietly than in the larger retort before employed; the liquid was also reduced by boiling to the same volume in every experiment, and thus the causes of variation as much as possible avoided. The designation of each column remains the same as in Table 1.

TABLE 2.*

No.	I.	II.	III.	IV.	
(1)	20 cbc.	70·2	5 cbc.	68·1	
(2)	20 „	68·3	5 „	68·0	
(3)	20 „	68·3	5 „	67·9	
(4)	20 „	66·9	5 „	68·0	
(5)	20 „	66·2	5 „	68·0	
(6)	20 „	66·2	5 „	68·0	Mean 68·00

Hence we may conclude:—

(1.) That the residual liquid obtained by boiling aqueous nitric acid of various degrees of concentration under the ordinary atmospheric pressure possesses a constant composition.

(2.) That the liquid thus obtained contains 68·0 per cent. of real acid, and that, therefore, the proportion between acid and water cannot be represented by any simple atomic relation, the formula $HNO_6 + 3HO$ requiring 70·0 per cent. of HNO_6.*

The boiling-point of the acid, containing 68·0 per cent., was found to be 120°·5 C., under a barometric pressure of $0^m·735$; its specific gravity at 15°·5 C. was shown to be 1·414 as a mean of two determinations.

Distilled at other temperatures, the relation of real acid to water will, if the phenomenon of constant boiling-point depends altogether on physical causes, be found to be a different one. In the following experiments, aqueous nitric acid of various degrees of strength, was distilled under diminished atmospheric pressure, effected by placing the acid in a retort, the neck of which, drawn out and bent at an acute angle, passed through a solid caoutchouc stopper into a large bolt-head of 20 litres capacity, furnished with a divided manometer-tube, and communicating with the cylinder of a large air-pump. By this means the acid could be distilled under any wished-for pressure less than that of the atmosphere; by cooling the bolt-head, and by having a large absorbent surface of caustic soda in the interior of the flask, it was easy to keep the mercury in the manometer tube to within 5 millimetres of the required height during the whole course of the distillation. Table 3 contains the results of a series of such experiments; Column I, gives the pressure in millimetres of mercury, under which the distillation took place (*i. e.*, the barometric pressure,—the height of the mercurial column in the manometer-tube); Column II, the volumes of liquid employed; Column III, the percentage of real acid contained in this liquid; Column IV, the volume remaining after distillation; Column V, the percentage of real acid contained in the residual liquid.

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* Calculated percentage composition of the hypothetical hydrates of nitric acid:—

	(1st)	(2nd)	(3rd)	(4th)
$H.NO_6$ . .	87·5	77·8	70·0	63·6
HO . .	12·5	22·2	30·0	36·4
	100·0	100·0	100·0	100·0

TABLE 3.

No.	I.	II.	III.	IV.	V.
(1)	75 mm.	150 cbc.	69·9	50 cbc.	66·7
(2)	50 „	20 „	68·3	5 „	67·2
(3)	75 „	150 „	66·9	50 „	66·7
(4)	68 „	20 „	66·5	5 „	66·8
(5)	75 „	20 „	66·2	5 „	66·5
(6)	75 „	120 „	65·1	30 „	66·7
(7)	150 „	150 „	66·9	50 „	67·6

Although showing a maximum difference of 1 per cent., owing to the acid being mechanically carried over by the irregular percussive ebullition, which it is impossible to prevent when nitric acid is heated under a diminished pressure, the results obtained are still sufficiently accurate to prove, that under a pressure of about 70 millimetres of mercury, when the boiling-point lies between 65° and 70°, a liquid possessing a constant mean composition of 66·7 per cent. of HNO_6 is obtained, whilst under a pressure of 150 millimetres, the equilibrium occurs when the percentage of acid reaches 67·6.

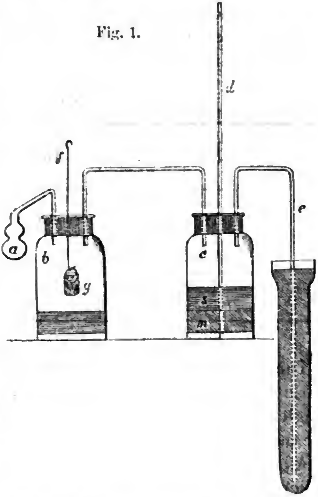


Fig. 1.

The distillation of nitric acid under pressures greater than that of the atmosphere, is accompanied by considerable experimental difficulties, owing to the impossibility of bringing the acid into contact with mercury. These difficulties were overcome by employing the following arrangement:—The bulb-retort (*a*) Fig. 1, containing the acid, was connected by means of a solid caoutchouc stopper with a strong bottle (*b*), of one litre capacity, containing some dilute nitric acid; through the stopper passes a second tube, communicating with another similar bottle (*c*) containing mercury (*m*) and a strong solution of caustic soda (*s*); a divided manometer tube (*d*) dipped into the mercury, and a third tube (*e*) passing through the stopper of the bottle (*c*) could be placed to any required depth into a reservoir of mercury. The bottle (*b*) being immersed in cold water, the increase of pressure was attained by pushing the glass bucket (*g*), filled with pieces of marble, into the dilute acid, by means of the stiff iron wire (*f*), working perfectly air-tight through the caoutchouc stopper. As soon as the mercury in the manometer tube had attained the wished-for height, and the gas issued from the extremity of the tube (*e*) under the mercury, a portion of the acid in the retort was distilled over, and the residue afterwards analyzed. By withdrawing the marble from the acid and again immersing it when required, the pressure was kept tolerably constant during the whole course of the experiment. The numbers in the following Table show, that distilled under a mean pressure of 1,220 millimetres of mercury, beyond which it was found inconvenient to operate, the composition of the residual liquid reached 68·6 per cent. of real acid, being a deviation from the acid distilled under ordinary pressures of 0·6 per cent.

TABLE 4.

No.	I.	II.	III.	IV.	V.
(1)	1260 mn.	20 cbc.	70·5	5	68·8
(2)	1210 ,,	20 ,,	68·3	5	68·7
(3)	1190 ,,	20 ,,	68·0	5	68·4

Mean 1220. Mean 68·6

The numbers in the columns have the same signification as those in Table 3, except in the first, in which the sum of the heights of the barometric column and the column of mercury in the manometer tube is given.

As it has thus been shown that aqueous nitric acid is a liquid which does not give rise on distillation to bodies possessing a simple atomic constitution, but that for each temperature a liquid having a constant composition is obtained, it appeared of interest to determine for lower temperatures the composition of the acid unalterable by vaporization.

For this purpose, air, completely dried over sulphuric acid and phosphoric anhydride, was passed through the nitric acid contained in the burette-shaped vessel, Fig. 2, until no further change in composition was observed. The requisite temperature was obtained by immersing the burette in a large water-bath, the heat of which was kept constant, a weighed U-tube, containing phosphoric anhydride, being placed between the burette and the drying apparatus, to ensure all absence of moisture. Experiments thus conducted for every temperature, show that a point is reached at which the composition of the aqueous acid undergoes no further change by vaporization. In Table 5, Column I gives the percentage of real acid in the liquid before the experiment; Column II, the percentage after the experiment; Column III, the fraction of the original volume of acid remaining after the experiment; Column IV, the duration of the experiment in hours.

Fig. 2.

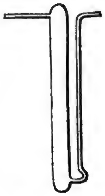


TABLE 5.

Passage of dry air through acid at 100° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·2	$\frac{1}{4}$	2 hrs.
(2)	64·9	66·1	$\frac{2}{3}$	1 ,,
(3)	64·9	66·3	$\frac{1}{4}$	3 ,,

Passage of dry air through acid at 60° C.

(1)	68·0	66·9	$\frac{1}{2}$	6 hrs.
(2)	66·9	65·7		9 ,,
(3)	65.7	65·2		30 ,,
(4)	65·2	64·9		9 ,,
(5)	64·9	64·8		20 ,,
(6)	64·9	64·8	$\frac{3}{4}$	8 ,,
(7)	64·8	64·5	$\frac{1}{2}$	9 ,,
(8)	64·5	64·4	$\frac{1}{3}$	9 ,,
(9)	64·0	64·5	$\frac{1}{2}$	8 ,,
(10)	64·5	64·5	$\frac{1}{4}$	6 ,,

Passage of dry air through acid at mean temp. of 13° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·2	½	48 hrs.
(2)	66·2	65·2		24 „
(3)	65·2	64·0		24 „
(4)	64·0	64·0		48 „
(5)	64·0	64·0		24 „
(6)	63·0	63·3		48 „
(7)	63·9	63·9		72 „
(8)	63·9	64·0		48 „

It is thus seen—(1.) That weak or strong aqueous nitric acid through which dry air is passed at 100°, attains a constant composition of 66·2 per cent. of real acid. (2.) That when air is passed through the same acid at 60°, the composition becomes constant at 64·5 per cent.; and (3.) That at the ordinary atmospheric temperatures—in mean 13°—the equilibrium is reached when the liquid contains 64·0 per cent. of real acid.

The ease with which strong nitric acid is decomposed, even at temperatures below its boiling point, is well known. It seems to be impossible to prepare the real acid HNO_6 by employing the usual method of distillation, rectification over sulphuric acid, and volatilization of the oxides of nitrogen by means of a current of dry air or carbonic acid. None of the chemists who have worked upon this subject appear to have had the real acid, and I have also failed to obtain it, although every care to ensure absence of moisture was taken; one colourless acid contained 99·8 per cent. of real acid, another 99·47 per cent. The former, nearly anhydrous acid, not only suffered decomposition on boiling, as is seen by reference to Table 1, but underwent alteration when a current of air perfectly dried over a large quantity of phosphoric anhydride was passed through the liquid at 15°. In seven hours, after which time three-fourths of the acid had been volatilized, the percentage of real acid had sunk to 98·77. This shows that nitric acid (HNO_6) undergoes decomposition, not only when vaporized at the boiling point, but also at the ordinary atmospheric temperatures.

II.—*Sulphuric Acid.*

We owe to Marignac the interesting and important observation, that real sulphuric acid (HSO_4) cannot be obtained by the distillation either of a weaker aqueous acid or of a stronger fuming acid. The real acid can only be prepared by crystallisation, and, on boiling, is decomposed into anhydride, which is seen in the receiver, and a weaker acid remaining in the retort. Marignac showed that this weaker residual acid boils at 338° C, without undergoing change; and he further proved that aqueous sulphuric acid of every degree of concentration, whether containing more or less water than the real acid (HSO_4), attains this constant composition on boiling. From four separate determinations, Marignac found that this residual liquid contained 98·70 per cent. of real acid.

The following determinations have confirmed in every particular Marignac's conclusions. The analyses were made by weighing out the requisite quantities of pure fused carbonate of sodium, the exact point of neutrality being estimated by addition of small volumes of standard alkali and acid of well-established strengths.

(1.) Pure strong sulphuric acid, containing 93·4 per cent. of real acid, was distilled in a retort, until two-thirds of the liquid had been volatilized. The liquid remaining in the retort contained 98·7 per cent. of real acid.

(2.) An acid containing 98·37 per cent. of HSO_4 was distilled in a small retort, until one-fifth of the original volume remained. The residue contained 98·32 per cent. of HSO_4.

(3.) An acid containing 98·37 per cent. of HSO_4 was boiled down in a porcelain capsule to one-third of its original volume. The residual liquid contained 98·45 per cent. of real acid.

(4.) An acid containing 100·33 per cent. of HSO_4, and fuming in contact with the air at ordinary temperatures, was boiled down to one-eighth of its orignal volume. The residual liquid contained 98·8 per cent. of real acid.

(5.) Another portion of the same fuming acid, which a second analysis showed to contain 100·34 per cent. HSO_4, was boiled to one-fourth of its original volume. The residual liquid contained 98·40 per cent. of real acid.

It thus appears not only that aqueous sulphuric, like aqueous nitric acid, attains an unalterable composition not corresponding to any definite hydrate, on distillation under the ordinary atmospheric pressure; but we also notice, what is very remarkable, that both the real acids, HNO_6 and HSO_4, bodies which possess in other respects the characteristics of well-defined chemical compounds, are decomposed on boiling, yielding that aqueous acid which remains unchanged at the temperature of ebullition.

III.—*Hydrochloric Acid.*

Bineau found that aqueous hydrochloric acid boiled under the ordinary atmospheric pressure, attained a composition of 20·2 p.c. of HCl, corresponding exactly* to the formula $HCl+16HO$, and this liquid he conceived to be a definite hydrate. In a research upon the absorption of hydrochloric acid and ammonia in water, published in vol. XII, page 128, of the Journal of the Chemical Society, which I made in conjunction with Mr. Dittmar, this result of Bineau's was, to a certain extent, confirmed, inasmuch as the acid of constant composition obtained by ebullition under the ordinary atmospheric pressure was found to contain 20·24 per cent. of HCl; but it was at the same time shown, that distilled under other pressures, or vaporized at other temperatures, this acid was decomposed, other liquids of constant composition being then produced, and the conclusion was therefore drawn that this hydrate has no real existence. The following Table 6, extracted from the above-mentioned memoir, gives the relation between the pressure under which the acid is distilled, and the composition of the constant liquid. The Column P shows the pressure in metres of mercury, under which aqueous hydrochloric acid must be distilled to attain the constant composition given in the next column.

TABLE 6.

Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.
0·05	23·2	0·6	20·7	1·3	19·3	2·0	18·5
0·1	22·9	0·7	20·4	1·4	19·1	2·1	18·4
0·2	22·3	0·76	20·24	1·5	19·0	2·3	18·3
0·3	21·8	0·8	20·2	1·6	18·9	2·4	18·1
0·4	21·4	0·9	19·9	1·7	18·8	2·5	18·0
0·5	21·1	1·0	19·7	1·8	18·7		
		1·1	19·5	1·9	18·6		
		1·2	19·4				

Hence it is evident:—(1.) That there exists for each pressure a corresponding aqueous hydrochloric acid, which undergoes no change in composition when distilled under this pressure, and therefore has a constant boiling point. (2.) That the composition of these aqueous acids is different for each pressure, a gradual change in pressure being accompanied by a gradual alteration in the percentage of hydrochloric acid.

When aqueous hydrochloric acid is vaporized by passing a current of dry air through the liquid at a given temperature, a similar point is reached beyond which no decomposition occurs. Table 7 contains the interpolated values obtained from the experimental results given in the original paper. The first column gives the temperatures; the second column gives the percentage of HCl contained in the acid, unalterable at the corresponding temperature.

TABLE 7.

T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.
0°	25·0	30°	24·1	60°	23·0	90°	21·4
5°	24·9	35°	23·9	65°	22·8	95°	21·1
10°	24·7	40°	23·8	70°	22·6	100°	20·7
15°	24·6	45°	23·6	75°	22·3		
20°	24·4	50°	23·4	80°	22·0		
25°	24·3	55°	23·2	85°	21·7		

IV. *Hydrobromic Acid.*

Löwig first observed that water saturated at the ordinary atmospheric temperature with hydrobromic acid gas loses acid when boiled, and that water containing but little gas in solution loses water under similar circumstances. **Bineau** showed that the composition of the acid obtained by boiling was constant, and, his experiments proving that such acid contained from 46·1 to 47·4 per cent. of HBr, he concluded that on distillation the hydrate containing 10 atoms of water is formed. According to theory, this hydrate should contain 47·38 per cent. of HBr, when the equivalent of bromine is taken as 80. On exposing aqueous acid of the above strength in a closed vessel over dried potash, or on passing a current of dry air through the acid, **Bineau** found that the residual liquid contained from 48·7 to 51·7 per cent. of hydrobromic acid; this he assumes to be a hydrate containing 9 atoms of water, composed theoretically of equal weights of water and real acid (HBr.)

For the purpose of determining the exact relation of the composition of aqueous hydrobromic acid to the temperature of ebullition, the acid was prepared by shaking together pure bromine, water, and phosphorus, added in small pieces from time to time, until the liquid became colourless, the strong fuming solution being freed by distillation from phosphorus and phosphoric acid. The pure and colourless acid thus prepared was diluted to a given extent with water; and as soon as the percentage of real acid (HBr), which the diluted liquid contained had been estimated by accurate volumetric analysis with silver, it was boiled in a bulb-tube retort, under the ordinary atmospheric pressure, until a certain portion of the acid had distilled over, when the composition of the residue was determined by exact analysis with silver.

In Table 8 are seen the results of eight such distillations with aqueous hydrobromic acids of various degrees of concentration: Column I gives the barometric pressure under which the acid boiled; Column II, the volume in cubic centimetres of acid employed: Column III, the percentage of HBr contained in the original liquid; Column IV, the volume in cubic centimetres of acid remaining in the retort after the distillation; and Column V, the percentage of HBr contained in the residual liquid, being the mean of two analyses, which generally differed only in the second decimal place.

TABLE 8.

No.	I.	II.	III.	IV.	V.
	m.				
(1)	0·752	25 cbc.	45·54	8 cbc.	47·38
(2)	0·752	50 „	45·58	8 „	47·39
(3)	0·753	50 „	47·30	25 „	47·78
(4)	0·762	25 „	47·65	12 „	47·86
(5)	0·753	20 „	47·78	5 „	47·61
(6)	0·752	12 „	47·87	6 „	47·73
(7)	0·752	50 „	49·00	8 „	47·71
(8)	0·762	25 „	49·51	10 „	47·84

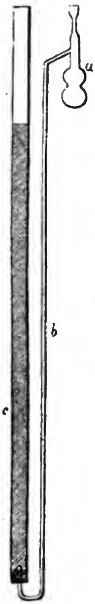
If the distillations are conducted under the same conditions, the compositions of the residual acids are identical (see Nos. 4 and 8); if the physical conditions (barometric pressure, and volume of liquid employed) are different, the acid may vary in composition about 0·1 or 0·2 per cent., as is seen in one or two of the numbers. From the foregoing experiments we see that aqueous hydrobromic acid when boiled under the ordinary atmospheric pressure of 0·76 of mercury, attains a fixed composition of 47·8 per cent. of real acid, or contains 0·5 per cent. more acid than Bineau's hypothetical hydrate. Under these circumstances it was found to boil constantly at 126°C. That the point of constant composition which aqueous hydrobromic acid attains on vaporization, is not solely dependent upon chemical attractions, but is mainly influenced by physical circumstances, is still more distinctly seen on examining the change which the aqueous acid undergoes when a current of dry air is passed through the liquid at a constant temperature. Through a liquid containing 47·65 per cent. of real acid, dry air was passed at the temperature of 16° for 50 hours; after the lapse of this time, the strength of the acid reached 51·8 per cent., and after the air had passed for 30 hours longer, the liquid contained 51·65 per cent. of real acid as a mean of two analyses, and had, therefore, attained the point of constant composition. Hence it is clear that neither of the supposed hydrates of hydrobromic acid has a real existence. In order to determine the point of equilibrium for other temperatures, perfectly dry air was passed through the acid at 100° contained in the burette Fig. 2, and the alteration which the liquid underwent was determined. The following results were obtained :—

Dry air passed through aqueous acid at 100° C.

										P.C. real acid.
(1)	1 vol. acid	containing	48·0	p. c.	when reduced to	⅛	vol.	contained		49·59
(2)	,,	,,	48·05	,,	,,	⅔	,,	,,		49 07
(3)	,,	,,	49·10	,,	,,	½	,,	,,		49·35
(4)	,,	,,	50·10	,,	,,	⅓	,,	,,		49·35

The aqueous acid was also distilled under a greatly increased pressure by help of the arrangement represented in Fig. 3. (*a*) Fig. 3 is a small bulb blown before the lamp, to which is fused the glass tube (*b*), communicating by a solid caoutchouc stopper with

Fig. 3.



the divided manometer tube (*c*), containing mercury. After the tube (*c*) had been filled with mercury to the requisite height, the acid was placed in the bulb, and then the drawn-out end closed before the blowpipe. The distillation was now commenced and continued until the acid had diminished to a given volume, when the pressure was read off from the difference of height of the columns of mercury in the two tubes. For the purpose of obtaining the boiling point of the acid under these circumstances, a thermometer was inserted into the bulb-tube, and the apparatus made air-tight by a joint of caoutchouc and lead-foil carefully wrapped with copper-wire. Under a total pressure of 1·952 metres of mercury, the acid boiled at 153° C; analysis of the residual acid gave the following results:—

(1) Acid containing 48·0 per cent. left after distillation a residual liquid containing 46·30 per cent. of real acid (HBr).

(2) Acid containing 46·07 per cent. left after distillation a liquid containing 46·36 per cent. of real acid.

v. *Hydriodic Acid.*

Bineau concluded that the liquid of constant boiling point obtained by distilling a diluted or a saturated aqueous solution of hydriodic acid was composed of 11 atoms of water to one of real acid (HI). The residual acid contained, according to his experiments, from 56·3 to 57·2 per cent. of hydriodic acid, whilst, according to calculation, the 11-atom hydrate requires 56·39 per cent. of real acid. Aqueous hydriodic acid was prepared by leading into distilled water the gas evolved by heating a mixture of 20 parts of pure iodine, 14 parts of iodide of potassium and 1½ parts of phosphorus mixed with a little water. The acid thus obtained of any requisite degree of concentration was perfectly colourless when preserved out of contact with air, and although the acid was always distilled in a current of hydrogen, it still became slightly coloured, but was not decomposed to such an extent as to affect the results of the analysis. The composition of the acid before and after the distillation was determined by volumetric analysis with silver; the results of these determinations, as is seen by reference to the following numbers, are closely concordant; care, however, must always be taken to have excess of silver present at the commencement of the analysis, otherwise some iodine is liberated by the free nitric acid.

TABLE 9.

Distillation of aqueous hydriodic acid under the ordinary atmospheric pressure.

Volume of liquid employed in each experiment 25 cbc.

" " remaining after each distillation 13 cbc.

	Percentage of real acid taken.	Percentage of real acid in the residue.
(1)	56·50	57·03
(2)	56·70	56·93 56·94 56·90
(3)	57·24	57·03
(4)	57·17	57·16 57·03 57·12
(5)	58·76	57·03 57·10

Hence it is seen that the acid of constant composition which is obtained when aqueous hydriodic acid is boiled under the ordinary atmospheric pressure, contains 57·00 per cent. of real acid, and cannot, therefore, be considered to be a definite hydrate of hydriodic acid. The boiling point of this acid was found to be 127° C. under a barometric pressure of 0·774 metre. In order to ascertain the point of equilibrium for other temperatures, aqueous hydriodic acid was vaporized in a current of dry hydrogen gas at the temperatures of 16° and 100°. Table 10 gives the results of such experiments.

TABLE 10.

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at ordinary atmospheric temperature.

	Temp.	Duration of the experiment.	Percentage of real acid taken.	Percentage of real acid in residue.
(1)	15°	32 hours	57·0	59·44
(2)	15°	41 „	59·44	60·36 60·33
(3)	17°	15 „	60·03	60·27
(4)	17°	15 „	60·27	60·42 60·39
(5)	19°	10 „	60·21	60·68
(6)	19°	6 „	60·68	60·49 60·42

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at 100° until half the liquid was volatilized.

	Percentage of real acid taken.	Percentage of real acid in residue.
(1)	56·98	58·49
(2)	59·78	58·26
(3)	58·21	58·24 58·20

VI. *Hydrofluoric Acid.*

Aqueous hydrofluoric acid, when boiled under the ordinary atmospheric pressure, attains, according to Bineau, a constant composition corresponding to the formula $HFl + 4HO$, and containing 35·9 per cent. of anhydrous acid.

In order to verify this assertion, pure aqueous hydrofluoric acid was prepared by leading the gas evolved from a strong acid heated in a platinum retort into water, also contained in a platinum vessel; the acid thus obtained being then boiled under the atmospheric pressure, and the quantity of acid contained in the residual liquid determined, by throwing the acid, weighed in a platinum capsule, into a vessel containing an excess of standard soda solution. The quantity of free soda was estimated by adding a slight excess of test acid, and the point of neutrality was considered to be reached when the litmus again became coloured blue on adding soda solution drop by drop in the cold. The results of a series of experiments thus conducted are seen in Table 11, in which Column I gives the volume of acid before boiling; Column II the percentage of HFl contained in the liquid before boiling; Column III the volume of HFl after boiling; and Column IV the percentage of HFl contained in the liquid after boiling.

TABLE 11.

I.	II.	III.	IV.	I.	II.	III.	IV.
80 cbc.	1·2	6 cbc.	5·8	12 cbc.	36·9	6	37·4 37·2
80 „	6·2	40 „	11 8	24 „	38·1	12	36·1 36·0
35 „	11·8	6 „	29·0	12 „	38·1	6	36·8 36·7
80 „	16·5	6 „	35·4 34·9	24 „	38·9	12	38·1 38·2
20 „	32·0	2 „	35·2	40 „	39·0	20	35·1 36·2 36 1
60 „	35·4	80 „	36·4 36·2	80 „	41·6	40	39·1 39·0
80 „	36·4 36·8	60 „	37 0 37·1 37·1				
24 „	26·5	12 „	37·6 37·5				

From these experiments it is evident that when aqueous hydrofluoric acid is boiled in platinum vessels under the ordinary atmospheric pressure, it attains a composition varying from 36 to 38 per cent. of HFl. The great differences observed arising from the impossibility of keeping the physical conditions constant, under which the ebullition takes place. We may take the mean 37·0 per cent. as representing pretty closely the composition of the acid unalterable by boiling in the air. If a true chemical compound between acid and water were thus produced, such large variations in the composition of the residual acid could not have been found. Vaporized at other temperatures, this constant hydrofluoric acid, containing 37·0 per cent. of HFl undergoes change. A portion of acid of the above strength, obtained by ebullition was placed in a platinum crucible over quick lime inside a leaden exsiccator closed with a lid having a sulphuric acid joint. After standing at a temperature of 15° C. for 4 days, the acid was found to contain, in two analyses, 36·4 and 36·6 per cent. of HFl; after remaining 4 days longer at the same temperature, the liquid contained 33·5 per cent. of acid; and when the acid had been standing for 2 more days at the same temperature over quick lime, it was found to contain 32·5 and 32·7 per cent. of acid. A weaker acid was next vaporized under like conditions; an acid containing 31·6 per cent. of HFl placed over quick lime at 15° attained, after 2 days, a composition of 32·1 per cent., and after a further exposure in the exsiccator for 4 days, two analyses showed that it contained 32·4 and 32·3 per cent. of HFl.

I beg to thank my assistant Mr. Schorlemmer for the able help which he has given me in carrying out the foregoing experiments.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting, March 30, 1860.

Professor **Brodie**, President, in the Chair.

The following **Report** was read by the President:—

The number of Fellows of the Chemical Society has, during the last year, continued to increase; 26 new Fellows have been elected, 3 Fellows have resigned, and three have been removed by death.

At the last Anniversary Meeting, March, 1859,

The number of Fellows was	302
The increase has been	21
The number of present Fellows is . .	323

The number of Associates at the last meeting was 9, and 3 have been since elected.

It appeared desirable to the Council to connect with the Society a greater number of the distinguished Chemists of foreign countries. The number of foreign members has hitherto been limited to 25. Application was made to the Society for power to increase this number to 40. At the present moment, however, it has not been thought expedient to add more than 6 names to the list, making in all 30 Foreign Members. The names thus added are the well-known names of **Berthelot**, **Deville**, **Frémy**, **Fritzsche**, **Mulder**, and **Peligot**.

The Council have ever regarded the formation of a Library of Chemical Works, as one of the most important objects to which the funds of the Society could be devoted, and they are especially desirous to render it at all times accessible and serviceable to the Fellows. They believed that these ends would be promoted by the appointment of a permanent Librarian; this office has been undertaken by Mr. Watts, a gentleman who is familiar with the literature of the science. Mr. Watts is at present engaged in preparing a new catalogue of the books.

The following papers have been read at the Meetings of the Society, since the Anniversary Meeting of 1859:—

"On the action of Boracic Acid upon the salts of the more volatile acids at high temperatures," by Mr. A. Norman Tate.

"On Boric and Silicic Acids," by Dr. Odling.

"On the action of Hydrochloric Acid upon Sulphide of Mercury in the presence of certain other substances," by Mr. F. Field.

"On the absorption of Ammonia and Hydrochloric Acid by water," by Dr. Roscoe.

"On Bases produced by Nitrous Substitution," by Mr. S. C. Wood.

"On the commercial estimation of Nitre," by Mr. J. S. Blockley.

"On the manufacture of Sulphate of Copper," by Mr. J. S. Blockley.

"On the saline atomic volume of Lithium," by Dr. Odling.

"On the action of Boracic Acid upon the Carbonates of the Alkaline Earths," by Prof. Bloxam.

"On the combination of Potassium with Carbonic Oxide," by Prof. Brodie.

"Remarks on the immediate source of the Carbon exhaled by the lungs," by Dr. Edward Smith.

"On the Crystalline Hydrates of Baryta and Strontia," by Prof. C. L. Bloxam.

"Description of an hermetically sealed Barometer," by Mr. Richard Adie.

"Note on the purification of Esculin and Paviin," by Prof. Stokes.

"On the action of Pentachloride of Phosphorus on Tartaric Acid," by Messrs. Perkin and Duppa.

"On the Vapour-density of Ethylenamine," by Dr. Hofmann.

"On the formation of Starch," by Dr. Moldenhauer.

"On the application of Electrolysis to the detection of the poisonous metals in mixtures containing organic matter," by Prof. Bloxam.

"On the Carbonates of Alumina and the Sesquioxides of Chromium and Iron," by Mr. James Barratt.

"On refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of Coinage," by Robert Warington.

"On certain sources of loss of precious metal in some operations of assaying," by Mr. G. H. Makins.

"On an Iron Sand from New Zealand," by Dr. J. H. Gladstone.

"On the composition of Air from Mont Blanc," by Dr. E. Frankland.

"On Biniodacetic Acid," by Messrs. Perkin and Duppa.

"On some derivatives from the Olefines," by Dr. Guthrie.

"On New Zealand Iron Sand," by Mr. E. Riley.

"On the action of Chloride of Ethyl upon Ammonia," by Mr. Grooves.

The following discourses have been delivered:—

"On Polyatomic Alcohols," by Dr. Debus.

"On Graphite," by Prof. Brodie.

"On Gas Analysis," by Prof. Williamson.

During the present year the Society has lost by death three of its Fellows, Mr. Jacob Bell, Mr. Reginald Morley, and Dr. George Wilson, Professor of Technology at Edinburgh. It is the custom to give a brief account of the lives of those Fellows who are thus lost to the Society.

Mr. Jacob Bell was born in Oxfordshire, in the year 1810. His father was the founder of the important Pharmaceutical establishment with which his name is thus connected, and at 17 years of age he was apprenticed to his father's firm. In the intervals of business he still found time for self-improvement, and attended the lectures on Chemistry at the Royal Institution, and on the practice of Physic at King's College. He had also a decided taste for art, and received lessons on Painting from his friend the Acadamician, Mr. H. P. Briggs. This taste led him in later years to acquire a valuable collection of paintings, chiefly of the artists of the English school. This collection he bequeathed to the British Nation.

As the chief founder of the Pharmaceutical Society, Mr. Jacob

Bell had the strongest claims to the gratitude of his profession and to the consideration of all interested in the application of Chemical science. The foundation of this Society was decided on at a public meeting held upon the 15th of April, 1841; but it was at meetings held at the house of Mr. Jacob Bell, that its constitution may truly be said to have been framed.

He was a member of the Council from the commencement of the Society, and rarely allowed any engagement to interfere with his attendance at its meetings. At his death he was its President. He also founded the Journal of the Pharmaceutical Society and Transactions, to which he made several literary communications, and to the support of which he liberally contributed.

These professional labours were not unappreciated by other countries. Mr. Bell was an honorary member of various foreign scientific societies. He was one of the original Fellows of the Chemical Society, and also a Fellow of the Linnean and Zoological Society, and of the Society of Arts.

With the view of furthering the interests he had so much at heart, Mr. Bell obtained a seat in Parliament, and in June, 1851, he moved for leave to bring in a Bill to regulate the qualification of Pharmaceutical Chemists, and for other purposes connected with Pharmacy, which, although modified in many important respects from its original form, passed into law.

Towards the end of the year 1858, Mr. Bell's health seriously declined. In the year 1854, owing to his exertions in public speaking, he contracted an ulceration of the tongue, from which he never thoroughly recovered. His death took place at Tunbridge Wells, on Sunday, the 12th of June, 1859.

Mr. Bell's was an useful and honourable life. He laboured in the most disinterested manner, for a period of 18 years, to raise the standard of education in his profession, and to advance its true interests. Greatly through his efforts, relations were established between Practical Pharmacy and Scientific Chemistry, which in this country had never before existed, and the importance of which no Fellow of this Society can fail to recognize.

Robert Reginald Ingham Morley was born August 26th, 1826. A love of science, which was early manifested, induced him to enter himself as a student at the Royal College of Chemistry, in 1849, where he continued his studies for several years, and acted as Senior Assistant to Dr. Hofmann during the Winter Session of 1854.

In 1851, he communicated a paper to the Chemical Society "On Propione, the Ketone of Propionic Acid," and in 1854 communicated another paper to the Society (in conjunction with Mr. J. S. Abel) "On the action of Iodide of Ethyl on Toluidine."

He was for some time one of the Visitors of the Royal Institution.

Circumstances led him to give up the study of Chemistry as a profession, and subsequently his declining state of health prevented his making that use of his laboratory which his love of science would have prompted.

He died January 11th, 1860, aged 33.

George Wilson* was born in Edinburgh, on February 21, 1818. His parents, observing his quick sensibility and studious habits, determined to give him the best education in their power, and accordingly he passed through the High School of his native city, entered its University in 1833, and graduated in medicine six years afterwards. During this time, he showed himself a diligent and enthusiastic student of science, and his mind was directed more and more towards chemistry. After spending a session in London as assistant to Professor Graham, now the Master of the Mint, he commenced giving public lectures at Edinburgh. There he was attacked by a severe and lingering illness, from which he only recovered after the amputation of his left foot, and with a constitution so shattered that he never knew afterwards the blessing of sound health; yet he rose from his sick bed, not merely with his former elasticity of spirits and enthusiasm for science, but with a still nobler purpose in life, for thenceforward religion had the supreme control of his thoughts and actions. He devoted himself to teaching his favourite science, first in the School of Arts, then in the Veterinary College, and in the Extra-academical Medicine School, while he pursued various researches, and was a frequent writer on philosophical subjects. When it was proposed to form an Industrial Museum in the Scottish capital, he was selected as the Director, and to him was entrusted the collection of the specimens and models, a task on which he entered *con amore*, and performed well. In 1855 he was also appointed to the newly formed Regius Professorship of Technology, and he gave courses of lectures illustrated by the collection he was engaged in amassing.

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* The obituary notice of Professor Wilson has been kindly communicated by Dr. J. H. Gladstone.

But his labours were interrupted by frequent attacks of illness; his life became every year more precarious; he declined higher honours; and lecturing till within four days of the close of his life, he died on November 22, 1859. His funeral was a public one, attended by multitudes of all classes, his fellow-professors, and pupils, the townspeople who had listened to his popular lectures, the artizans whose affections he had won during his technological inquiries, and a large number of private friends to whom he was endeared by the freshness of his genius, the liveliness and wit of his discourse, the unselfishness and amiability of his character, and the genuineness of his piety.

It was as an expounder of science rather than as a discoverer that Dr. Wilson excelled; yet, exclusive of lectures and larger works, he published about thirty papers on subjects connected with Chemistry, General Physics, or Physiology. Some of these are to be found in our Memoirs or Quarterly Journal, others in the Edinburgh Philosophical Transactions, or elsewhere. Many of these communications have for their object the enforcement and further illustration of the views of other observers, and the inventing of crucial experiments for deciding between rival hypotheses. He boldly commenced with an "Experimental demonstration of the existence of Haloid salts in solution;" he then exploded the reputed conversion of Carbon into Silicon; but his most complete research of a chemical nature was that into the occurrence of Fluorine in the animal, vegetable, and mineral kingdoms, on which he published a series of papers. His researches on colour-blindness belong of course to another branch of science. He was particularly fond of tracing the history of inventions (as that of the air-pump), and he wrote several monographs on eminent chemists, besides his larger work, the "Life of Cavendish." But Professor Wilson's chief strength lay in explaining newly discovered scientific truths, and rendering them attractive by copious illustrations. Hence his popularity as a lecturer, and success as a writer. His little book on Chemistry, in Chambers's Educational Course, has attained a sale of twenty-four thousand; and his treatise on the Electric Telegraph, his "Five gateways of knowledge," and other small publications, have done much to diffuse a taste for experimental philosophy.

The Society then proceeded to the election of the Council and Officers for the ensuing year (for the List, see page 94 of this volume.)

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. **Cr.**

Date		£	s.	d.	£	s.	d.
1859. March 26.	To Cash in hand				519	5	4
July	,, Half-Year's Dividend on £450 3 per cent. Consols				6	12	3
1860. March.	,, Ditto ditto ditto				6	7	9
,,	,, Sundry Receipts from 25th March, 1859, to 24th March, 1860, as below—						
	Life Compositions	40	0	0			
	Admission Fees	64	0	0			
	Resident Members' Subscription previous to 1859................	10	0	0			
	Non-Resident ditto ...	16	0	0			
	Resident ditto for 1859 ...	32	0	0			
	Non-Resident ditto ,, ...	67	0	0			
	Resident ditto for 1860 ...	196	0	0			
	Non-Resident ditto ,, ...	89	0	0			
	Non-Resident ditto for 1861 ...	1	0	0			
					515	0	0
					£1047	5	4

Date		£	s.	d.	£	s.	d.
1860. March 24.	By Editor's Salary	50	0	0			
	,, ditto Translating	2	5	0			
	,, ditto Honorarium	10	0	0			
					62	5	0
	,, Printing Journal..................................				201	12	4
	,, Librarian's Salary to 1 Jan., 1860				15	0	0
	,, Collector's Commission				25	15	0
	,, Clerk				2	0	0
	,, T. Hux, Cleaning and Attendance, from March, 1859 to March, 1860				20	0	0
	,, Petty Expenses, as per Book				5	4	10
	,, Gate Porter...				1	1	0
	,, Royal Society, Share of Tea Expenses				17	17	0
	,, Subscription to Cavendish Society				1	1	0
	,, Books and Magazines				13	7	6
	,, Bookbinding				6	9	6
	,, Stamps, Postage, Envelopes, Stationery, Cab Hire, &c.				8	11	5
	,, Clock (C. Frodsham)............................				11	0	0
					391	4	7
1859. May 9.	,, Purchase of £100 3 per cent. Consols......				90	17	6
					482	2	1
1860. March 24.	,, Balance at Coutts's	515	3	3			
,, ,,	,, Ditto in Cash	50	0	0			
					565	3	3
					£1047	5	4

ASSETS.

	£	s.	d.
Balance in Cash	565	3	3
Invested in 3 per cent Consols ...	450	0	0
	£1,015	3	3

Examined and found correct, **W. H. THORNTHWAITE,**
W. H. PERKIN,
E. A. HADOW, } *Auditors.*

April, 5, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

Dr. Thomas Andrews delivered a discourse on "Ozone."

The following donations have been received:—

"Annales de Chimie" (1789 to 1805), 55 volumes: from Dr. R. D. Thomson.

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt," No. 3, für 1859: from the Institute.

"Chemical News," Nos. 13, 14, 15: from the Publishers.

"Journal of the Society of Arts," Nos. 380, 381, 382: from the Society.

"Journal of the Photographic Society" for March, 1860: from the Society.

"Literary Gazette," Nos. 89, 90: from the Publishers.

"On the Composition of the Photographic Image," by John Spiller, Esq.: from the Author.

April 19, 1860.

Robert Warington, Esq., in the Chair.

The following were elected Fellows of the Society:—

M. J. Stark, Esq., Norwich; J. A. R. Newlands, Esq., 19, West-square, Southwark; J. McDonnell, Esq., 71, Great Strand-street, Dublin; C. E. Long, Esq., Westcroft-place, Hammersmith; F. Sutton, Esq., Norwich.

The following papers were read:—

"On the artificial production of Tartaric Acid," by Messrs. Perkin and Duppa.

"On Crystallized Potassium and Sodium," by Mr. C. E. Long.

"On the History of Cinnamic Acid," by Mr. D. Howard.

"On the action of Sodium on Iodide of Methyl," by Messrs. Wanklyn and Buckheisen.

The following donations have been received:—

"Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg," Tome I., Feuilles 1—9: from the Academy.

"American Journal of Science and Arts," March, 1860: from the Editors.

"Canadian Journal," March, 1860: from the Editors.

"Atlantis," No. V.: from the Catholic University of Ireland.

"Two Orations delivered before the Academy of Sciences at Munich:" from the Academy.

"Report of Experiments with different Manures on Permanent Meadow Land," by J. B. Lawes, Esq., F.R.S., and Dr. J. H. Gilbert, F.R.S.: from the Authors.

May 3, 1860.

Professor Brodie, President, in the Chair.

William Proctor, Esq., Petergate, York, was elected a Fellow of the Society.

Dr. J. H. Gladstone delivered a discourse "On Circular Polarization."

The following donations have been received:—

"Transactions of the Royal Society of Edinburgh," Vol. XXII., Part 1.

"Proceedings of the Royal Society of Edinburgh," Session 1858–59: from the Society.

"Pharmaceutical Journal" for May, 1860: from the Editors.

"Chemical News," Nos. 16—21: from the Publishers.

"Journal of the Franklin Institute" for February, 1860: from the Institute.

"Journal of the Photographic Society" for April, 1860: from the Society.

"Literary Gazette," Nos. 91—94: from the Publishers.

"Journal of the Society of Arts," Nos. 383—387: from the Society.

May 17, 1860.

Robert Porrett, Esq., Vice-President, in the Chair.

The following papers were read:—

"On Zinc-methyl," by Mr. J. A. Wanklyn.
"On the Stibethyls and Stibmethyls," by G. B. Buckton.
"On some derivatives from the Olefines," by Dr. Guthrie.

The following donations have been received:—

"Proceedings of the Academy of Natural Sciences of Philadelphia," Nos. 1—5, for 1860: from the Academy.

"Journal of the Society of Arts," No. 388, 389, 390: from the Society.

"Journal of the Franklin Institute" for March and April, 1860: from the Institute.

"Quarterly Journal of the Geological Society," May, 1860: from the Society.

"Address delivered at the Anniversary Meeting of the Geological Society of London," February, 1860, by J. Phillips, Esq.: from the Author.

"Journal of the Photographic Society," May, 1860: from the Society.

"Chemical News," Nos. 22, 23: from the Publishers.

June 7, 1860.

Professor Brodie, President, in the Chair.

Dr. Frankland delivered a discourse on Organo-metallic bodies.

The following donations have been received:—

"Denkschriften der kaiserlichen Akademie der Wissenschaften (mathematisch-naturwissenschaftliche Klasse). Band. XVII."

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, No. 10—28."

"Register zu den Banden XXI bis XXX:"

from the Academy.

"Jahresbericht für Meteorolgie und Erdmagnetismus. Band VI für 1854."

"Almanach der kaiserlichen Akademie der Wissenschaften für 1849:"

from the Academy.

"Journal of the Society of Arts, Nos. 391—393:" from the Society.

"Chemical News, Nos. 24—26:" from the Publishers.

"Pharmaceutical Journal for June, 1860:" from the Editor.

"Literary Gazette, Nos. 95—98:" from the Publishers.

"Elements of Chemistry," by William Allen Miller, M.D. Part I, "Chemical Physics:" from the Author.

"Experimental Inquiry into the Composition of some of the Animals fed and slaughtered for Human Food," by J. B. Lawes, Esq., F.R.S., and Dr. J. H. Gilbert, F.R.S.: from the Authors.

"Repertory of Patent Inventions," 13 volumes;

"Newton's London Journal of Arts and Sciences:"

from Messrs. De La Rue.

June 21, 1860.

Thomas Graham, Esq., F.R.S., in the Chair.

The following papers were read:—

"On Baudrimont's Protosulphide of Carbon," by Lyon Playfair, C.B., F.R.S.

"On the composition of Hydrated Acids of Constant Boiling point," by H. E. Roscoe, Ph.D.

"On Acetoxybenzamic Acid, an isomer of Hippuric Acid," by G. C. Foster, Esq.

"On the employment of Saccharate of Lime as a Normal Alkaline Solution in Volumetric Analysis," by F. Maxwell Lyte, Esq.

The following donations have been received:—

"Philosophical Transactions," from Part II for 1854 to Part II for 1859: from the Royal Society.

"Observations made at the Magnetical and Meteorological Observatory at St. Helena," Vol. II.: presented by order of the British Government.

"Monthly Notices of the Royal Astronomical Society," No. 7: from the Society.

"Chemical News," Nos. 27, 28: from the Publishers.

"Twenty-seventh Annual Report of the Royal Cornwall Polytechnic Society:" from the Society.

"Journal of the Society of Arts," Nos. 394, 395: from the Society.

"Literary Gazette," Nos. 99—103: from the Publishers.

"Journal of the Photographic Society," June 1860: from the Society.

"Journal of the Franklin Institute," May, 1860: from the Institute.

"On the Alloys of Copper and Zinc," by F. H. Storer: from the Author.

"Photographs of Fluorescent Substances, showing the small Chemical effect of the Light reflected from them:" from Dr. J. H. Gladstone.

XIX.—*On Organo-metallic Bodies.*

A Discourse delivered to the Members of the Chemical Society of London,

By Dr. E. Frankland, F.R.S.

Although organo-metallic bodies, as a distinct class of organic compounds, are, with one exception, the creation of the last ten years, yet the derivatives of these bodies have been known for a much longer period. From the time that an organic acid was first united with a metallic base, these organic compounds containing metals date their existence. It is true that such compounds containing a metallic constituent have not been regarded from this point of view; but a little consideration will serve to show that they stand in the same relation to organo-metallic bodies in the strict sense of the term, as the ethers, alcohols, acids, and numerous other organic families occupy with regard to the alcohol-radicals from which they are derived. Thus zinc-ethyl yields by oxidation ethylate of zinc;

$$\underbrace{ZnC_4H_5}_{\text{Zinc-ethyl.}} + O_2 = \underbrace{ZnO, C_4H_5O}_{\text{Ethylate of zinc.}}$$

a body which, although unknown until formed by this reaction, has undoubted and well-known analogies in the ethylates of potash and soda.

By suitable processes of oxidation, ethylate of zinc may be converted into acetate of zinc.

$$\underbrace{ZnO, C_4H_5O}_{\text{Ethylate of zinc.}} + O_4 = \underbrace{C_4H_3ZnO_4}_{\text{Acetate of zinc.}} + H_2O_2$$

The ethyl-compounds of potassium and sodium also pass through analogous phases of oxidation.

Again potassium-ethyl and sodium-ethyl, under the influence of carbonic acid, yield the propionates of potash and soda:

$$\underbrace{KC_4H_5}_{\text{Potassium-ethyl.}} + C_2O_4 = \underbrace{C_6H_5KO_4}_{\text{Propionate of potash.}}$$

$$\underbrace{NaC_4H_5}_{\text{Sodium-ethyl.}} + C_2O_4 = \underbrace{C_6H_5NaO_4}_{\text{Propionate of soda.}}$$

The same result may also probably be reached by two distinct stages, viz., first by the conversion of potassium-ethyl and sodium-ethyl into the ethylates of potash and soda:

$$\underbrace{KC_4H_5}_{\text{Potassium-ethyl.}} + O_2 = \underbrace{C_4H_5O,\ KO}_{\text{Ethylate of potash.}}$$

and secondly by the action of carbonic oxide upon these bodies:

$$\underbrace{C_4H_5KO_2}_{\text{Ethylate of potash.}} + C_2O_2 = \underbrace{C_6H_5KO_4}_{\text{Propionate of potash.}}$$

The second stage of this conversion has not yet been experimentally realized, but Berthelot's ingenious production of formiate of potash from carbonic oxide and hydrate of potash exhibits an homologous reaction.

These examples serve to point out the relations existing between organo-metallic bodies in the usual acceptation of the term, and that far more numerous class of derivatives to which the same name might without impropriety be applied; and it is now only necessary to remark that the present discourse will be confined to the consideration of organo-metallic bodies in the usual and more restricted sense of the term.

Formation of Organo-metallic Bodies.

Organo-metallic bodies admit of being produced by a great variety of processes; but these numerous methods of formation, with very few exceptions, admit of being grouped under four heads.

1. *Formation by union of the organic radical in statu nascenti with the metal.*

Upon this method depends the production of *zinc-ethyl*, the reaction being usually expressed by the following equation:

$$\underbrace{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + 4Zn = \underbrace{\left.\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right\} Zn_2}_{\text{Zinc-ethyl.}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

It is, however, very doubtful whether this equation correctly expresses the actual change which occurs in the production of zinc-ethyl. It has long been known that this body is found in a free state, in very small quantity only, amongst the products of the reaction of zinc upon iodide of ethyl, but that there exists amongst these products a crystalline body which contains zinc, ethyl, and iodine, and which may be regarded as formed according to the equation :

$$\underset{\text{Iodide of ethyl.}}{\underline{\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Zn_2 = \underset{\text{Ethiodide of zinc.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}}}$$

This compound is decomposed at about 150° C, yielding iodide of zinc and zincethyl :

$$\underset{\text{Ethiodide of zinc.}}{\underline{2Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}} = \underset{\text{Zincethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

Contemporaneously with the first of the above reactions, there occur others in which ethyl, hydride of ethyl, and ethylene are produced. The separation of ethyl in this reaction is doubtless due to the direct action of zinc upon iodide of ethyl :

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Zn_2 = \underset{\text{Ethyl.}}{\underline{\left.\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right\}}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

whilst the appearance of the secondary products, ethylene and hydride of ethyl, results from the action of the ethiodide of zinc upon iodide of ethyl :

$$\underset{\text{Ethiodide of zinc.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}} + \underset{\text{Iodide of ethyl.}}{\underline{\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} = \underset{\text{Hydride of ehtyl.}}{\underline{\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}}} + \underset{\text{Ethylene.}}{\underline{C_4H_4}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

a view which is supported by the behaviour of sodium-ethyl in contact with iodide of ethyl.*

$$\underset{\text{Potassium-ethyl.}}{\underline{K_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}} + \underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} = \underset{\text{Ethylene.}}{\underline{2\,C_4H_4}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}}} + 2\,KI$$

Notwithstanding the intermediate stage just indicated in the production of zinc-ethyl, the final result of the reaction is correctly expressed in the first of the above equations.

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* Proceedings of Royal Soc., vol. ix, p. 345.

Zinc-methyl and *zinc-amyl* are produced in a perfectly analogous manner, but no attempt has yet been made to form the corresponding compounds of the remaining alcohol-radicals.

The same method of formation yields *cadmium-ethyl,*[*] when iodide of ethyl is digested with cadmium at a temperature of from 100° to 150° C.

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Cd_4 = \underset{\text{Cadmium-ethyl.}}{\underline{Cd_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}} + 2\left.\begin{matrix}Cd\\ I\end{matrix}\right\}$$

In this case also there appears to be an intermediate stage in the process, probably quite analogous to that noticed in the production of zinc-ethyl.

The temperature at which the ethiodide of cadmium thus formed is decomposed (177° C.) is considerably higher than that required for the decomposition of the corresponding zinc-compound, in consequence of which a small proportion only of cadmium-ethyl is obtained, the remainder being broken up into other products. This circumstance has hitherto prevented the complete investigation of cadmium-ethyl. The experiments of Wanklyn however scarcely permit its existence to be doubted.

No other organo-cadmium compounds have been formed.

Treated with iodide of ethyl, magnesium gives *magnesium ethyl,*[†] the reaction commencing briskly at ordinary temperatures, but requiring a heat of 120° C to 130° C for its completion:

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Mg_4 = \underset{\text{Magnesium-ethyl.}}{\underline{Mg_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}} + 2\left.\begin{matrix}Mg\\ I\end{matrix}\right\}$$

The homologous reaction with iodide of methyl appears also to yield *magnesium-methyl.*[‡]

Similarly treated, aluminum yields at temperatures from 100° to 130° C, *aluminium-ethyl* and *aluminium-methyl.*[§]

$$3\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\} + Al_4 = \left(Al_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\ I\\ I\end{matrix}\right.\right)$$

$$3\left.\begin{matrix}C_2H_3\\ I\end{matrix}\right\} + Al_4 = \left(Al_2\left\{\begin{matrix}C_2H_3\\ C_2H_3\\ C_2H_3\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\ I\\ I\end{matrix}\right.\right)$$

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[*] Wanklyn, Chem. Soc. Qu. J., ix, 193.

[†] Cahours, Ann. Ch. Phys. [3], lviii, 17.

[‡] Ibid, p. 19.

[§] Ibid, p. 20.

Double compounds of aluminium-ethyl and aluminium-methyl with the iodide of aluminium are here formed, and the organo-aluminium bodies have not yet been obtained with certainty free from iodide of aluminium.

Glucinum-ethyl[*] appears also to be formed under similar circumstances, but its existence has not yet been confirmed by analysis.

Organo-compounds of Tin.—Although these bodies can be obtained by other processes, the general method we are now considering is doubtless the most convenient mode of producing most of them. Tin is capable of forming three distinct classes of binary inorganic compounds which may be represented by the following general formulæ:

$$Sn_2\left\{\begin{array}{l}R\\R\end{array}\right. \qquad Sn_2\left\{\begin{array}{l}R\\R\\R\end{array}\right. \qquad Sn_2\left\{\begin{array}{l}R\\R\\R\\R\end{array}\right.$$

This threefold atomic character of the metal tin renders the result of its action upon the iodides of the alcohol-radicals considerably less simple than those we have hitherto considered. Without taking into account compounds to which a still more complex constitution has been assigned, the existence of the following series of organo-metallic bodies containing tin has been established:[†]

1st Series.	2nd Series.	3rd Series.
$Sn_2\left\{\begin{array}{l}R+\\R+\end{array}\right.$	$Sn_2\left\{\begin{array}{l}R+\\R+\\R+\end{array}\right.$	$Sn_2\left\{\begin{array}{l}R+\\R+\\R-\end{array}\right.$
4th Series.	**5th Series.**	**6th Series.**
$Sn_2\left\{\begin{array}{l}R+\\R+\\R+\\R+\end{array}\right.$	$Sn_2\left\{\begin{array}{l}R+\\R+\\R+\\R-\end{array}\right.$	$Sn_2\left\{\begin{array}{l}R+\\R+\\R-\\R-\end{array}\right.$

The second and fourth of these series have not yet been produced by the method we are now considering.

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[*] Cahours, Ann. Ch. Phys. [3], lviii, 22.

[†] In these formulæ R+ represents a positive organic radical, and R— a negative radical: no negative organic radical, as such, has yet been introduced into these compounds.

First Series. *Stannous ethide* $\left(Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.\right)$ is produced in small quantities by the action of heat upon a mixture of iodide of ethyl and tin:

$$\underset{\text{Iodide of ethyl.}}{\underline{2 \left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}} + Sn_4 = \underset{\text{Stannous ethide.}}{\underline{Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}} + Sn_2 \left\{\begin{matrix} I \\ I \end{matrix}\right.$$

Stannous methide is doubtless formed under similar conditions:

$$\underset{\text{Iodide of methyl.}}{\underline{2 \left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}} + Sn_4 = \underset{\text{Stannous methide.}}{\underline{Sn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}} + Sn_2 \left\{\begin{matrix} I \\ I \end{matrix}\right.$$

The third series of stann-organic compounds are formed by the following reactions:

$$\underset{\text{Iodide of methyl.}}{\underline{2 \left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}} + Sn_3 = \underset{\text{Dimethiodide of tin.}}{\underline{Sn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ I \end{matrix}\right.}} + SnI$$

$$\underset{\text{Iodide of ethyl.}}{\underline{2 \left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}} + Sn_3 = \underset{\text{Diethiodide of tin.}}{\underline{Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ I \end{matrix}\right.}} + SnI$$

Fifth Series. The following chemical changes express the mode of formation of compounds belonging to this series:

$$\underset{\text{Iodide of methyl.}}{\underline{3 \left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}} + Sn_4 = \underset{\text{Stannic Iodotrimethide.}}{\underline{Sn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ I \end{matrix}\right.}} + Sn_2 \left\{\begin{matrix} I \\ I \end{matrix}\right.$$

$$\underset{\text{Iodide of ethyl.}}{\underline{3 \left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}} + Sn_4 = \underset{\text{Stannic Iodotriethide.}}{\underline{Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ I \end{matrix}\right.}} + Sn_2 \left\{\begin{matrix} I \\ I \end{matrix}\right.$$

Sixth Series.—The most abundant products of the action of tin upon the iodides of the alcohol-radicals belong to this series; indeed, if the action be produced by light instead of heat, this series of bodies is formed almost to the complete exclusion of the others. It is necessary, however, to remark that the materials exposed to light should be completely excluded from atmospheric oxygen, otherwise the liquid assumes an orange colour, and the action is so effectually arrested that an exposure for several months to sunlight, concentrated by a parabolic mirror, will scarcely produce any appreciable change. The following reactions explain the formation of bodies belonging to this series:

$$\underset{\text{Iodide of methyl.}}{\underline{2\left.\begin{array}{c}C_2H_3\\ I\end{array}\right\}}} + Sn_2 = \underset{\text{Stannic dimethiodide.}}{\underline{Sn_2\left\{\begin{array}{r}C_2H_3\\ C_2H_3\\ I\\ I\end{array}\right.}}}$$

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{array}{c}C_4H_5\\ I\end{array}\right\}}} + Sn_2 = \underset{\text{Stannic diethiodide.}}{\underline{Sn_2\left\{\begin{array}{r}C_4H_5\\ C_2H_3\\ I\\ I\end{array}\right.}}}$$

$$\underset{\text{Iodide of amyl.}}{\underline{2\left.\begin{array}{c}C_{10}H_{11}\\ I\end{array}\right\}}} + Sn_2 = \underset{\text{Stannic diamyliodide.}}{\underline{Sn_2\left\{\begin{array}{r}C_{10}H_{11}\\ C_{10}H_{11}\\ I\\ I\end{array}\right.}}}$$

It is evident that three series of tin-compounds are still wanting to complete the category, viz.:

$$Sn_2\left\{\begin{array}{ll}R & +\\ R & -\end{array}\right. \qquad Sn_2\left\{\begin{array}{ll}R & +\\ R & -\\ R & -\\ R & -\end{array}\right. \qquad Sn_2\left\{\begin{array}{ll}R & +\\ R & -\\ R & -\end{array}\right.$$

It is somewhat remarkable that no organo-tin compounds containing only one equivalent of positive radical, have hitherto been produced. The inference to be drawn from this, that such bodies do not exist, must be checked by the fact that no special attempts have yet been made to form them.

Organo-compounds of Mercury.—The reaction of mercury upon the iodides of the alcohol-radicals gives rise to two series of organic compounds, the general formulæ of which may be thus written:

$$\underset{\text{1st Series.}}{\mathrm{Hg}\left\{\begin{matrix}\mathrm{R}\ + \\ \mathrm{R}\ -\end{matrix}\right.} \qquad\qquad \underset{\text{2nd Series.}}{\mathrm{Hg}\left\{\begin{matrix}\mathrm{R}\ + \\ \mathrm{R}\ +\end{matrix}\right.}$$

The first series only of these bodies can be produced by the general mode of formation now under consideration; but the members of the second series are readily obtained by the action of an organo-zinc compound upon those of the first.

For the production of the first series of these bodies, the action of light is essential, except in the case of mercuric iodo-allide, no elevation of temperature being capable of producing the chemical change. The following equations sufficiently exhibit the nature of the reaction:

$$\underset{\text{Iodide of methyl.}}{\underline{\left.\begin{matrix}C_2H_3 \\ I\end{matrix}\right\}}} + \mathrm{Hg} = \underset{\text{Mercuric iodomethide.}}{\underline{\mathrm{Hg}\left\{\begin{matrix}C_2H_3 \\ I\end{matrix}\right.}}}$$

$$\underset{\text{Iodide of ethyl.}}{\underline{\left.\begin{matrix}C_4H_5 \\ I\end{matrix}\right\}}} + \mathrm{Hg} = \underset{\text{Mercuric iodoethide.}}{\underline{\mathrm{Hg}\left\{\begin{matrix}C_4H_5 \\ I\end{matrix}\right.}}}$$

$$\underset{\text{Iodide of allyl.}}{\underline{\left.\begin{matrix}C_6H_5 \\ I\end{matrix}\right\}}} + \mathrm{Hg} = \underset{\text{Mercuric iodo-allide.}}{\underline{\mathrm{Hg}\left\{\begin{matrix}C_6H_5 \\ I\end{matrix}\right.}}}$$

For the production of the methyl-compound, bright sunlight may be employed; but the reaction for the ethyl-body must be conducted in diffused daylight only, otherwise no organo-metallic compound will be produced, the ethyl being eliminated chiefly as such, but partly, also, as hydride of ethyl and ethylene:

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5 \\ I\end{matrix}\right\}}} + \mathrm{Hg}_2 = 2\mathrm{HgI} + \underset{\text{Ethyl.}}{\underline{\left.\begin{matrix}C_4H_5 \\ C_4H_5\end{matrix}\right\}}}$$

$$\underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5 \\ I\end{matrix}\right\}}} + \mathrm{Hg}_2 = 2\mathrm{HgI} + \underset{\text{Hydride of ethyl.}}{\underline{\left.\begin{matrix}C_4H_5 \\ H\end{matrix}\right\}}} + \underset{\text{Ethylene.}}{\underline{C_4H_4}}$$

In addition to these bodies, compounds containing arsenic and antimony can also be produced by this general mode of formation; but they are obtained with greater facility by the second method, which will now be described.

2. *Formation of organo-metallic bodies by the action of the respective metals alloyed with potassium or sodium upon the iodides of the alcohol-radicals.*

The principles involved in this second general mode of production are essentially similar to those in the first, but there is here less tendency to form compounds containing negative as well as positive radicals. This method, although not capable of such general application, is more especially adapted to the formation of the organic compounds of the polyatomic metals. The simultaneous production of an organo-potassium or sodium compound need not be feared, since such compounds cannot exist in the presence of the iodides of the alcohol-radicals.

This mode of formation will be sufficiently illustrated by the following reactions:

Arsenic-compounds.

$$\underbrace{2\left.\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{I}\end{matrix}\right\}}_{\text{Iodide of methyl.}} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right. = \underbrace{\mathrm{As}\left\{\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{C_2H_3}\end{matrix}\right.}_{\text{Cacodyl.}} + \mathrm{2NaI}$$

$$\underbrace{2\left.\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{I}\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right. + \underbrace{\mathrm{As}\left\{\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{C_4H_5}\end{matrix}\right.}_{\text{Ethyl-cacodyl.}} + \mathrm{2NaI}$$

$$\underbrace{3\left.\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{I}\end{matrix}\right\}}_{\text{Iodide of methyl.}} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{Na}\end{matrix}\right. = \underbrace{\mathrm{As}\left\{\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{C_2H_3}\\ \mathrm{C_2H_3}\end{matrix}\right.}_{\text{Trimethylarsine.}} + \mathrm{3NaI}$$

$$\underbrace{3\left.\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{I}\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{Na}\end{matrix}\right. = \underbrace{\mathrm{As}\left\{\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{C_4H_5}\\ \mathrm{C_4H_5}\end{matrix}\right.}_{\text{Triethylarsine.}} + \mathrm{3NaI}$$

$$\underbrace{4\left.\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{I}\end{matrix}\right\}}_{\text{Iodide of methyl.}} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{Na}\end{matrix}\right. = \underbrace{\mathrm{As}\left\{\begin{matrix}\mathrm{C_2H_3}\\ \mathrm{C_2H_3}\\ \mathrm{C_2H_3}\\ \mathrm{C_2H_3}\\ \mathrm{I}\end{matrix}\right.}_{\text{Iodide of tetramethylarsonium.}} + \mathrm{3NaI}$$

$$\underset{\text{Iodide of methyl.}}{\underline{4\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + As\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Iodide of tetraethylarsonium.}}{\underline{As\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\\ C_4H_5\\ I\end{matrix}\right.}}} + 3NaI$$

Antimony-compounds.

$$\underset{\text{Iodide of methyl.}}{\underline{3\left.\begin{matrix}C_2H_3\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Trimethylstibine.}}{\underline{Sb\left\{\begin{matrix}C_2H_3\\ C_2H_3\\ C_2H_3\end{matrix}\right.}}} + 3NaI$$

$$\underset{\text{Iodide of ethyl.}}{\underline{3\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Triethylstibine.}}{\underline{Sb\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\end{matrix}\right.}}} + 3NaI$$

$$\underset{\text{Iodide of amyl.}}{\underline{3\left.\begin{matrix}C_{10}H_{11}\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Triamylstibine.}}{\underline{Sb\left\{\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\end{matrix}\right.}}} + 3NaI$$

$$\underset{\text{Iodide of methyl.}}{\underline{4\left.\begin{matrix}C_2H_3\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Iodide of tetramethylstibonium.}}{\underline{Sb\left\{\begin{matrix}C_2H_3\\ C_2H_3\\ C_2H_3\\ C_2H_3\\ I\end{matrix}\right.}}} + 3NaI$$

$$\underset{\text{Iodide of ethyl.}}{\underline{4\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Iodide of tetrethylstibonium.}}{\underline{Sb\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\\ C_4H_5\\ I\end{matrix}\right.}}} + 3NaI$$

$$\underset{\text{Iodide of amyl.}}{\underline{4\left.\begin{matrix}C_{10}H_{11}\\ I\end{matrix}\right\}}} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = \underset{\text{Iodide of tetramylstibonium.}}{\underline{Sb\left\{\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\\ I\end{matrix}\right.}}} + 3NaI$$

Tin-compounds.

$$\underbrace{2\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix}Na\\Na\end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stannous-methide.}} + 2NaI$$

$$\underbrace{3\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix}Na\\Na\\Na\end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stann-sesquimethide.}} + 3NaI$$

$$\underbrace{4\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix}Na\\Na\\Na\\Na\end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stannic methide.}} + 4NaI$$

Analogous reactions also represent the formation of the corresponding compounds containing ethyl and amyl.

Lead-compound.

$$\underbrace{3\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Pb_2\left\{\begin{matrix}Na\\Na\\Na\end{matrix}\right. = \underbrace{Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Plumb-sesquiethide.}} + 3NaI$$

Bismuth-compound.

$$\underbrace{3\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Bi\left\{\begin{matrix}Na\\Na\\Na\end{matrix}\right. = \underbrace{Bi\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Bis-triethide.}} + 3NaI$$

Tellurium-compounds.

Organo-tellurium compounds are formed by a modification of this method, which consists in distilling telluride of potassium with sulphovinate of potash and its homologues.

$$\underbrace{2(C_2H_3O.SO_3 + KO.SO_3)}_{\text{Sulphomethylate of potash.}} + 2KTe = \underbrace{Te_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Tellurium-methyl.}} + 4(KO.SO_3)$$

The ethyl and amyl compounds are prepared by homologous reactions.

3. *Formation of organo-metallic bodies by the action of the zinc-compounds of the organic radicals upon the haloid compounds either of the metals themselves or of their organo-derivatives.*

For the production of organo-metallic bodies containing less positive metals than zinc, this method is perhaps not only the most convenient, but also capable of the most general application. Compounds containing mercury, tin, lead, antimony, and arsenic, have been thus produced, but it has failed when applied to the haloid compounds of copper, silver, and platinum, for although these bodies are violently acted upon, the organic group does not unite with the metals.

The following reactions represent the present state of our knowledge with regard to this method of formation:—

Mercury-compounds.

$$\underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} + Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{Hg \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Mercuric methide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} + 2Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{2Hg \left\{\begin{matrix} C_2H_3 \\ Cl \end{matrix}\right.}_{\text{Mercuric chloromethide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{Hg \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Mercuric ethide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} = 2Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{2Hg \left\{\begin{matrix} C_4H_5 \\ Cl \end{matrix}\right.}_{\text{Mercuric chlorethide.}} + 2ZnCl$$

Mercurous ethide and mercurous methide have not yet been obtained either by this or any other process. The instability of mercurous compounds, as seen in the inorganic oxide and iodide, is brought to a climax in organic mercurous compounds; the latter are instantly transformed into metallic mercury and the more stable organo-mercuric compounds. Thus, when zinc-ethyl acts upon mercurous chloride, the following change results:—

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2HgCl = \underbrace{Hg \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Mercuric ethide.}} + Hg + 2ZnCl$$

Tin-compounds.

$$\underbrace{2Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2 \left\{\begin{matrix} Cl \\ Cl \\ Cl \\ Cl \end{matrix}\right.}_{\text{Stannic chloride.}} = \underbrace{Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Stannic ethide.}} + 4ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic diethiodide.}} = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethide.}} + 2ZnI$$

$$\underbrace{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{2Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.}_{\text{Chlorotriethide of tin.}} + 6ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.}_{\text{Stannic dichlorethide.}} + 2ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + SnCl = \underbrace{\left.\begin{matrix}Zn\\Sn\end{matrix}\right\}\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincostannous ethide.}} + ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic di-iodoethide.}} = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stannic diethylomethide.}} + 2ZnI$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\I\end{matrix}\right.}_{\text{Stannic iodo-trimethide.}} = \underbrace{2Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethylotrimethide.}} + 2ZnI$$

Lead-compound.

The following is the only reaction which has hitherto been effected by the method which we are now considering:—

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2PbCl = \underbrace{Pb\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Plumbic ethide.}} + Pb + 2ZnCl$$

Antimony-compounds.

$$\underbrace{3Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + 2Sb\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{2Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Trimethylstibine.}} + 6ZnCl$$

$$\underset{\text{Zinc-ethyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + 2Sb\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. = \underset{\text{Triethylstibine.}}{\underline{2Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}} + 6ZnCl$$

Arsenic-compounds.

$$\underset{\text{Zinc-methyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} + 2As\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. = \underset{\text{Trimethylarsine.}}{\underline{2As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}} + 6ZnCl$$

$$\underset{\text{Zinc-ethyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + 2As\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. = \underset{\text{Triethylarsine.}}{\underline{2As\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}} + 6ZnCl$$

4. *Formation of organo-metallic bodies by the displacement of a metal in an organo-metallic compound by another and more positive metal.*

Wanklyn, to whom we are indebted for this mode of formation, regards this displacement of one metal by another as a case of true electrolytic decomposition. He thinks that in zinc-ethyl, for instance, ethyl is the electro-negative and zinc the electro-positive member: sodium being more electro-positive than zinc, replaces the latter metal, and forms sodium-ethyl. But he supposes that where the original organo-metallic body contains a metal less electro-positive than the hydrocarbon radical, then the latter, and not the metal, would be eliminated by contact with a more positive metal. Cacodyl, for instance, when treated with sodium should give methyl and arsenide of sodium:

$$\underset{\text{Cacodyl.}}{\underline{As\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} + Na_2 = \underset{\text{Arsenide of sodium.}}{\underline{As\left\{\begin{matrix}Na\\Na\end{matrix}\right.}} + \underset{\text{Methyl.}}{\underline{\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}}}$$

This view, the correctness of which is more than probable, is supported by the action of potassium and of zinc-ethyl upon ammonia:

$$\underset{\text{Ammonia.}}{\underline{2N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.}} + K_2 = \underset{\text{Potassamide.}}{\underline{2N\left\{\begin{matrix}K\\H\\H\end{matrix}\right.}} + H_2$$

$$\underset{\text{Ammonia.}}{\underline{2N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.}} + \underset{\text{Zincethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} = \underset{\text{Zincamide.}}{\underline{2N\left\{\begin{matrix}Zn\\H\\H\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

In accordance with this hypothesis, Wanklyn considers that the ethyl in sodium-ethyl would be displaced by copper, mercury, platinum, &c., and that sodium-ethyl is only in equilibrium with bodies, whose respective positions in the electrical scale are either both of them within, or both of them without, the space lying between the electro-positive sodium and the electro-negative ethyl.

This fourth mode of producing organo-metallic bodies has hitherto been applied only to the formation of sodium and potassium compounds, or rather double compounds of these bodies with zincethyl, according to the following reactions:

$$\underset{\text{Zincethyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + Na_2 = \underset{\text{Double compound of sodium-ethyl and zinc-ethyl.}}{\underline{\left(2Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + Na_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.\right)}} + Zn_2$$

$$\underset{\text{Zincethyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + K_2 = \underset{\text{Double compound of potassium-ethyl and zinc-ethyl.}}{\underline{\left(2Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + K_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.\right)}} + Zn_2$$

Sodium also displaces mercury from mercuric ethide: sodium-ethyl seems to be formed, but the exact nature of the reaction has not been ascertained.

Properties of Organo-metallic Bodies.

The organo-metallic compounds as a class are distinguished for the extraordinary energy of their affinities. With certain exceptions, presently to be noticed, their disposition to unite with negative elements increases with the positive character of the metal and with the smallness of the atomic weight of the alcohol-radical. Thus organo-potassium and sodium compounds possess more chemical energy than those of zinc, whilst the latter are more active than the compounds of arsenic, antimony, tin, or lead. Again, in the series belonging to each metal, the methylic compounds are more energetic than the ethylic ones, whilst the last greatly surpass the amylic compounds in this respect. But whilst these general principles govern the chemical energy of organo-metallic bodies, their effect appears to be modified by the degree of saturation in which the metal exists. Although this circumstance has hitherto received only very partial elucidation, yet we have evidence of its existence in the case of organo-tin compounds. Both stannous ethide and stannous methide combine directly with atmospheric oxygen, and the union takes place with tolerable rapidity; but neither stannic ethide nor stannic methide is in the least degree acted upon by free oxygen at ordinary temperatures; even iodine acts upon them with difficulty. This diminution of chemical energy in organo-stannic compounds cannot be ascribed to the mere influence of the additional weight of hydrocarbon which they contain, since stannous amylide readily unites with free oxygen at ordinary temperatures, although the single molecule of amyl which it contains is considerably heavier than the double atom of either methyl or ethyl present in the organo-stannic compounds just cited.

Organo-metallic compounds in a state of partial saturation play the part of compound radicals. They are uniatomic, biatomic, teratomic, or quadratomic, according to the number of molecules requisite to complete their saturation. On the other hand, organo-metallic bodies in a state of saturation never perform radical functions, they never undergo chemical change without decomposition. Thus zinc-ethyl, stannic ethide, mercuric ethide, and plumbic ethide all give substitution-products when they are chemically acted upon.

The description of the special properties of the organo-metallic bodies may be conveniently commenced with the most positive of the class, viz.:

*Potassium and sodium series.**—These bodies have not yet been isolated; they are known only in combination with the corresponding zinc-compounds. The double compound of sodium-ethyl and zinc-ethyl is the only one which has hitherto been submitted to analysis. Its formula is

$$2Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + Na_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$$

This compound first separates from its solution in zinc-ethyl as a transparent fluid, which after some time solidifies to a mass of large tabular crystals, fusing at 27° C., but when once fused remaining fluid at several degrees below that point. On the application of a moderate heat, gases are evolved, and a mixture of sodium and zinc without carbon is left behind. The double compound decomposes water with great violence, forming hydride of ethyl, and the hydrated oxides of zinc and sodium. The behaviour with negative elements has not yet been studied. Its most interesting reaction consists in the absorption of carbonic acid, which it transforms into propionic acid. The sodium-ethyl alone takes part in this reaction:*

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* Wanklyn, Proceedings of Roy. Soc., ix, 341.

$$\underset{\text{Sodium-ethyl.}}{\underline{Na_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} \quad - \quad 2C_2O_4 \quad = \quad \underset{\text{Propionate of soda.}}{\underline{2\left.\begin{matrix}C_6H_5O_2\\Na\end{matrix}\right\}O_2}}$$

A similar double compound containing ***sodium-methyl,*** as well as the potassium-compounds of ethyl and methyl, have been formed. They have not yet been completely investigated, but it is believed that their composition and properties are perfectly analogous to those of sodium-ethyl.

No compound of any of these bodies with a negative element has been obtained. Their action upon carbonic acid proves that they possess a still higher reducing power than the corresponding organo-zinc compounds, and they will therefore doubtless prove valuable agents for the substitution of positive groups for negative elements in cases where organo-zinc compounds fail to produce the desired effect.

Sodium-ethyl decomposes the iodides of the alcohol-radicals in the cold, with formation of iodide of sodium.†

$$\underset{\text{Sodium-ethyl.}}{\underline{Na_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Iodide of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}} = 2NaI + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}} + \underset{\text{Ethylene.}}{\underline{2\,C_4H_4}}$$

Owing to this behaviour, potassium and sodium compounds can only be prepared by method No. 4.

Magnesium series.‡—The compounds containing ethyl and methyl only have hitherto been examined, and the former alone submitted to analysis. These bodies possess a close similarity to organo-zinc compounds. They are very volatile colourless liquids, possessing a powerful alliaceous odour; are spontaneously inflammable, and decompose water with violence. They do not readily decompose the iodides of the alcohol-radicals, and can therefore be prepared by method No. 1. No compound of these bodies with negative elements has yet been produced. They are in the condition of chemical saturation. Further details of their properties are wanting.

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* Wanklyn, Chem. Soc. Qu. J., xi, 103.

† Frankland, Proceedings of Roy. Soc., ix, 345.

‡ Cahours, Ann. Ch. Phys., lviii, 17.

*Aluminium and Glucinum series.**—Like the organo-compounds of the alkaline metals, the aluminium and glucinum compounds have not yet been isolated with certainty; they are known only in combination with the iodides of the respective metals, and the composition of the ethyl and aluminium body only has been fixed by analysis. Its formula is

$$Al_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\I\\I\end{matrix}\right.$$

These double compounds possess great chemical energy; they are spontaneously inflammable, volatile liquids, which decompose water with explosive violence. They are attacked by zinc-ethyl, forming iodide of zinc and very inflammable liquids, which latter are believed to be the pure organo-compounds. They appear to be chemically saturated bodies, and therefore incapable of direct combination. Further details are wanting.

Zinc series.†—Three bodies belonging to this series are known, viz.:

Zinc-methyl	$Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Zinc-ethyl	$Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Zinc-amyl	$Zn_2\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.$

They are colourless, transparent, mobile, volatile, and odorous liquids, composed of four gaseous volumes of the hydro-carbon radical, and two volumes of zinc-vapour, the six volumes condensed to four. The methyl and ethyl compounds are spontaneously inflammable, burning with a greenish blue flame. All three are saturated compounds incapable of direct combination. In contact with water, they are instantly decomposed, with formation of oxide of zinc and hydride of the organic radical.

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* Cahours, Ann. Ch. Phys., lviii, 20.

† Frankland, Chem. Soc. Qu. J., ii, 297, and iii, 44; Phil. Trans., cxlii, 431, and cxlv, 259. Wanklyn, Chem. Soc. Qu. J., xiii, 124.

$$\underset{\text{Zinc-methyl.}}{\underline{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}Zn\\Zn\end{matrix}\right\}O_2 + \underset{\substack{\text{Hydride of}\\\text{methyl.}}}{\underline{2\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}Zn\\Zn\end{matrix}\right\}O_2 + \underset{\substack{\text{Hydride of}\\\text{ethyl.}}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc-amyl.}}{\underline{Zn_2\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}Zn\\Zn\end{matrix}\right\}O_2 + \underset{\substack{\text{Hydride of}\\\text{amyl.}}}{\underline{2\left.\begin{matrix}C_{10}H_{11}\\H\end{matrix}\right\}}}$$

Gradually treated with oxygen, so as to avoid too violent action, they form the respective zinc-alcohols.

$$\underset{\text{Zinc-methyl}}{\underline{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} + O_4 = \underset{\text{Methylate of zinc.}}{\underline{2\left.\begin{matrix}C_2H_3\\Zn\end{matrix}\right\}O_2}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + O_4 = \underset{\text{Ethylate of zinc.}}{\underline{2\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2}}$$

$$\underset{\text{Zinc-amyl.}}{\underline{Zn_2\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.}} + O_4 = \underset{\text{Amylate of zinc.}}{\underline{2\left.\begin{matrix}C_{10}H_{11}\\Zn\end{matrix}\right\}O_2}}$$

The action of iodine upon organo-zinc-compounds consists in the transformation of both their constituents into iodides.

$$\underset{\text{Zinc-methyl.}}{\underline{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} + I_4 = 2ZnI + \underset{\text{Iodide of methyl.}}{\underline{2\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}}$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + I_4 = 2ZnI + \underbrace{2 \left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_{10}H_{11} \\ C_{10}H_{11} \end{matrix}\right.}_{\text{Zinc-amyl.}} + I_4 = 2ZnI + \underbrace{2 \left.\begin{matrix} C_{10}H_{11} \\ I \end{matrix}\right\}}_{\text{Iodide of amyl.}}$$

Organo-zinc compounds behave in a manner exactly analogous in contact with the other halogens.

Reactions like the foregoing, point to the applicability of these compounds for effecting the substitution of positive groups for negative elements in compound bodies, an application which has not failed to attract the notice of chemists. In addition to the reactions of this class given above as examples of the formation of organo-metallic bodies by the third method, the following have been realized :

With Binoxide of Nitrogen.*

$$\underbrace{2(N_2O_4)}_{\substack{\text{Binoxide of} \\ \text{nitrogen.}}} + \underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} = \underbrace{2 \left.\begin{matrix} N_2C_2H_3O_2 \\ Zn \end{matrix}\right\} O_2}_{\substack{\text{Dinitro-methylate} \\ \text{of zinc.}}}$$

$$2(N_2O_4) + \underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} = \underbrace{2 \left.\begin{matrix} N_2C_4H_5O_2 \\ Zn \end{matrix}\right\} O_2}_{\text{Dinitro-ethylate of zinc.}}$$

It will be perceived that these reactions are the exact analogues of the one already mentioned in the sodium and potassium series, where carbonic acid, treated with sodium-methyl and sodium-ethyl, forms acetic and propionic acids. In fact, dinitro-methylic and dinitro-ethylic acids may be regarded as the analogues of acetic and propionic acid respectively; the nitrogen here sustaining a biatomic character, and replacing an equivalent amount of carbon.

With Sulphurous Acid.†

$$\underbrace{2(S_2O_4)}_{\text{Sulphurous acid.}} + \underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} + \underbrace{2 \left.\begin{matrix} S_2C_2H_3O_2 \\ Zn \end{matrix}\right\} O_2}_{\substack{\text{Methylodithionate} \\ \text{of zinc.}}}$$

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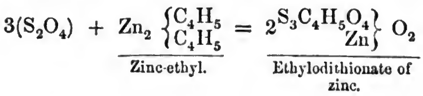
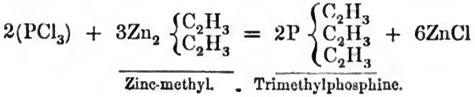
* Frankland, Phil. Trans., 1857, p. 59.

† Hobson, Chem. Soc. Qu. J., x, 55 and 243.

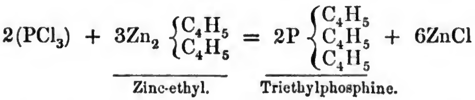


$$3(S_2O_4) + \underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} = \underset{\text{Ethylodithionate of zinc.}}{\underline{2\left.\begin{matrix}S_3C_4H_5O_4\\Zn\end{matrix}\right\}O_2}}$$

With Terchloride of Phosphorus.*

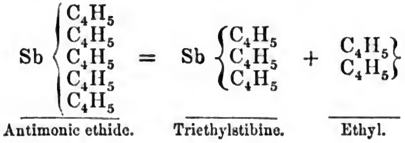


$$2(PCl_3) + \underset{\text{Zinc-methyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}} = \underset{\text{Trimethylphosphine.}}{\underline{2P\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}} + 6ZnCl$$



$$2(PCl_3) + \underset{\text{Zinc-ethyl.}}{\underline{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} = \underset{\text{Triethylphosphine.}}{\underline{2P\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}} + 6ZnCl$$

There is no apparent obstacle to this reaction being pushed to its extreme limit in the case of pentatomic bodies, such as phosphorus, arsenic, or antimony. Mr. Buckton has recently attempted this in the case of antimony; but although evidence of the existence of a pentethide of antimony was obtained, the body could not be isolated and its composition satisfactorily fixed. The great stability of the triatomic compounds of these bodies will probably present considerable difficulty in the way of obtaining pentatomic compounds of an exclusively positive character, such bodies being doubtless easily resolved into the more stable groupings represented in the following equation:



$$\underset{\text{Antimonic ethide.}}{\underline{Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}} = \underset{\text{Triethylstibine.}}{\underline{Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Ethyl.}}{\underline{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}}}$$

Whilst on the one hand, organo-zinc compounds are thus capable of effecting the substitution of their positive organic group for negative elements, they can, on the other hand, in certain cases replace hydrogen by zinc, forming, for instance, with ammonia and its homologues, a series of zincamides. In this direction the following reactions have been recorded.†

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* Hofmann and Cahours, Phil. Trans. for 1857, p. 578.

† Frankland, Proc. of Royal Soc., viii, 502.

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Ammonia.}}{\underline{2N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.}} = \underset{\text{Zincamide.}}{\underline{2N\left\{\begin{matrix}Zn\\H\\H\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Aniline.}}{\underline{2N\left\{\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right.}} = \underset{\text{Zincphenylimide.}}{\underline{2N\left\{\begin{matrix}C_{12}H_5\\Zn\\H\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Diethylamine.}}{\underline{2N\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right.}} = \underset{\text{Diethyl-zincamide.}}{\underline{2N\left\{\begin{matrix}C_4H_5\\C_4H_5\\Zn\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Oxamide.}}{\underline{N_2\left\{\begin{matrix}C_4O_4''\\H_2\\H_2\end{matrix}\right.}} = \underset{\text{Zincoximide.}}{\underline{N_2\left\{\begin{matrix}C_4O_4''\\Zn_2\\H_2\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}} + \underset{\text{Acetamide.}}{\underline{2N\left\{\begin{matrix}C_4H_3O_2\\H\\H\end{matrix}\right.}} = \underset{\text{Zinc-acetimide.}}{\underline{2N\left\{\begin{matrix}C_4H_3O_2\\Zn\\H\end{matrix}\right.}} + \underset{\text{Hydride of ethyl.}}{\underline{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}}$$

Of the same nature apparently is the reaction between zinc-ethyl and acetic anhydride.*

$$Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + \left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2 = \left.\begin{matrix}C_4H_2ZnO_2\\C_4H_2ZnO_2\end{matrix}\right\}O_2? + 2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$$

The members of the zinc-series unite with neutral salts to form compounds which have been but little examined. The following, however, are known :†

Dinitromethylate of zinc and zinc-methyl	$2\left.\begin{matrix}N_2C_2H_3O_2\\Zn\end{matrix}\right\}O_2 + Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Dinitroethylate of zinc and zinc-ethyl	$2\left.\begin{matrix}N_2C_4H_5O_2\\Zn\end{matrix}\right\}O_2 + Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$

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* When zinc-ethyl is added to acetic anhydride, torrents of pure hydride of ethyl are evolved; the other product of the reaction has not been examined.

† Frankland, Phil. Trans., 1857, p. 59.

Finally, it has been observed, that zinc-methyl when generated in contact with methylic or vinic ether, combines with these bodies, forming*

Methylate of zinc-methyl	$2\left(Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.\right) + \left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}O_2$
Ethylate of zinc-methyl	$2\left(Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.\right) + \left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$

Cadmium Series.†—Only one member of this series is known, and that very imperfectly. So far as its properties are made out, they appear to be perfectly analogous to those of the zinc compounds.

Tin Series.‡—A large number of organo-metallic bodies containing tin have been described. The existence of the following may be considered as clearly established.

a. Stannous compounds.

Stannous methide, or stanmethyl	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Stannous ethide or stanethyl	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$

b. Sesqui-compounds.

Sesquimethide of tin	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$
Sesquiethide of tin	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$
Dimethiodide of tin	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\I\end{matrix}\right.$
Diethiodide of tin	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\end{matrix}\right.$

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* Frankland, Phil. Trans., 1859, p. 412.

† Wanklyn, Chem. Soc. Qu. J., ix, 193.

‡ Frankland, Phil. Trans., 1852, p. 417, and Phil. Trans., 1859, p. 401. Cahours et Riche, Compt. rend., xxxv, 91, and xxxvi, 1001. Löwig, Ann. Ch. Pharm. lxxxiv, 308. A. Grimm, Ann. Ch. Pharm, xcii, 383, Buckton, Phil. Trans. for 1859, p. 423. Cahours, Ann. Ch. Phys., lviii, 22.

c. Stannic compounds.

Stannic methide	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$
Stannic ethide	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$
Stannic ethylomethide	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\end{matrix}\right.$
Stannic-ethylo-trimethide	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_5\end{matrix}\right.$
Stannic iodo-trimethide	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\I\end{matrix}\right.$
Stannic iodo-triethide	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.$
Stannic iodo-dimethide	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\I\\I\end{matrix}\right.$
Stannic iodo-diethide	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.$

It is scarcely necessary to observe that the iodine in the above compounds admits of replacement by any salt-forming radical and also by oxygen or sulphur.

Stannous compounds are oily liquids soluble in alcohol and ether, but insoluble in water, and possessing a pungent odour. They cannot be distilled without decomposition, being resolved into stannic compounds and metallic tin. They are in a state of partial chemical saturation only, and therefore perform the part of radicals, combining directly with chlorine, oxygen, &c., and forming well-marked bodies of great stability.

Stannous compounds are biatomic, and unite directly with free oxygen, chlorine, &c., to produce bodies of the stannic form. Thus stannous ethide forms with oxygen, stannic oxydiethide.

$$\underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\end{cases}}_{\text{Stannous ethide.}} + O_2 = \underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\O\\O\end{cases}}_{\text{Stannic oxydiethide.}}$$

Stannous compounds have never yet been observed to play a uniatomic part. No sesqui-compound has been directly formed from a stannous body; the latter, under the influence of iodine, oxygen, &c., seems to pass at once into the stannic form. It must be remarked, however, that no direct experiments have been made with a view of revealing any uniatomic attribute which may attach to stannous compounds.

Sesqui-compounds of the form $Sn_2\begin{cases}R+\\R+\\R+\end{cases}$ have hitherto been very little examined. They are oily liquids, uniting directly with negative radicals, forming an extensive series of compounds belonging to the stannic class, a considerable number of which have been studied. The following examples will serve to show the mode in which sesqui-compounds of this form pass into bodies of the stannic class:

$$\underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Sesquiethide of tin.}} + I = \underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\I\end{cases}}_{\text{Stannic iodotriethide.}}$$

$$\underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\I\end{cases}}_{\text{Stannic iodotriethide.}} + I_2 = \underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\I\\I\end{cases}}_{\text{Stannic iododiethide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

No reduction of a sesqui-compound to a stannous compound has yet been effected, although it can scarcely be doubted that an aqueous solution of diethiodide of tin, for instance, if treated with zinc, would yield stannous ethide. On the other hand, stannic ethide or methide in contact with iodine is transformed into a sesqui-compound, viz., diethiodide of tin:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stannic ethylo-dimethide.}} + I_3 = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\end{matrix}\right.}_{\text{Diethiodide of tin.}} + \underbrace{2\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}_{\text{Iodide of methyl.}}$$

Sesqui-compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.$ are very little known. In fact the diethiodide of tin, the production of which from stannic ethylodimethide has just been mentioned, is the only one known with certainty. It is a colourless mobile liquid, boiling with partial decomposition at 208° C., and possessing a most insupportable odour, resembling essential oil of mustard. Heated with excess of iodine, it is transformed into stannic iododiethide:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\end{matrix}\right.}_{\text{Diethiodide of tin.}} + I = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic iododiethide.}}$$

Stannic compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R+\\R+\end{matrix}\right.$ are colourless mobile liquids, possessing a slight ethereal odour. They are volatile without decomposition, and are very stable. Being in the condition of chemical saturation, they are incapable of direct combination. No body can act upon them without expelling one or more equivalents of positive radical. Thus, when heated with hydrochloric acid, stannic ethide yields stannic chlorotriethide and hydride of ethyl:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethide.}} + HCl = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.}_{\text{Stannic chlorotriethide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}}$$

With two equivalents of iodine, the reaction is :

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethide.}} + I_2 = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.}_{\text{Stannic iodotriethide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

And with four equivalents of iodine :

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethide.}} + I_4 = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic iododiethide.}} + \underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

Stannic compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R+\\R-\end{matrix}\right.$, commonly called compounds of sesquistanethyl, have been comparatively well studied. The oxides are, in the anhydrous condition, volatile, limpid, oily liquids which readily unite with water, forming crystalline hydrates which have a powerful alkaline reaction, and neutralize the strongest acids, forming an extensive series of salts. These salts are almost all soluble in water, readily crystallizable, and of a very pungent odour. The stannic iodotriethide and the stannic triethylosulphate may be adduced as examples of the haloïd and oxysalts respectively :

Stannic iodotriethide $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.$

Stannic triethylosulphate $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\SO_4\end{matrix}\right.$

Stannic compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R-\\R-\end{matrix}\right.$ have also been very completely investigated. The oxides are white amorphous powders, insoluble in water, alcohol, and ether. They dissolve in hydrochloric, hydriodic, and hydrobromic acids, forming colourless and inodorous salts, which crystallize in fine prisms. Most of the oxysalts can also be obtained in the crystalline form, either from aqueous or alcoholic solutions. The iodide and sulphate of stannic diethide, which may be regarded as representatives of the haloïd and oxysalts, have the following formulæ:

Stannic ethylodisulphate $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\SO_4\\SO_4\end{matrix}\right.$

Stannic iododiethide $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.$

Stannic compounds of this form are readily reduced to stannous compounds; thus, when a piece of zinc is plunged into a solution of stannic chlorodiethide, stannous ethide is produced:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.}_{\text{Stannic chlorodiethide.}} + Zn_2 = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannous ethide.}} + 2ZnCl$$

Bismuth Series.*—The following bodies belonging to this series have been described:

1. Bismuthous ethide $Bi\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$
2. Bismuthous dichlorethide $Bi\left\{\begin{matrix}C_4H_5\\Cl\\Cl\end{matrix}\right.$
3. Bismuthous di-iodoethide $Bi\left\{\begin{matrix}C_4H_5\\I\\I\end{matrix}\right.$
4. Bismuthous dioxyethide $Bi\left\{\begin{matrix}C_4H_4\\O\\O\end{matrix}\right.$?

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[*] Breed, Ann. Ch. Pharm., lxxxii, 106; Dünhaupt, Ann. Ch. Pharm., xcii, 371.

5. Double compound of bismuthous sulphide with bismuthic sulphotriethide $\left.\right\}$ $\mathrm{Bi}\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\S\\S\end{matrix}\right. + 2\mathrm{Bi}\left\{\begin{matrix}S\\S?\\S\end{matrix}\right.$

These bodies have as yet been but very imperfectly investigated. Bismuthous triethide is a colourless or slightly yellow mobile liquid, having an unpleasant odour like that of stibethine. Exposed to the air, it gives off dense yellow fumes, inflames spontaneously, and finally explodes. It is very instable, begins to decompose at 50° or 60° C., and explodes violently when heated to 150° C., a temperature still below its boiling point. No direct compound of this body has yet been obtained; it behaves like a chemically saturated substance, and when slowly oxidized in contact with water, yields alcohol and hydrated oxide of bismuth:

$$\underbrace{\mathrm{Bi}\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Bismuthous ethide.}} + 3\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 + O_6 = BiO_3,3HO + \underbrace{3\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}_{\text{Alcohol.}}$$

When an alcoholic solution of bichloride of mercury is added to an alcoholic solution of bismuthous ethide, mercuric ethochloride crystallizes out, whilst bismuthous dichlorethide remains in solution:

$$\underbrace{\mathrm{Bi}\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Bismuthous ethide.}} + 2HgCl_2 = \underbrace{\mathrm{Bi}\left\{\begin{matrix}C_4H_5\\Cl\\Cl\end{matrix}\right.}_{\text{Bismuthous dichlorethide.}} + \underbrace{2\mathrm{Hg}\left\{\begin{matrix}C_4H_5\\Cl\end{matrix}\right.}_{\text{Mercuric chlorethide.}}$$

From the bismuthous dichlorethide, the diiodide and dioxyethide are prepared by double decomposition, whilst the simultaneous action of sulphuretted hydrogen, water, bismuthous ethide, and atmospheric oxygen is said to produce the double compound of bismuthous sulphide and bismuthic sulphotriethide.

Lead Series.*—The following bodies only are known, the ethyl group alone having been explored:

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* Löwig, Ann. Ch. Pharm., lxxxviii, 318; Buckton, Phil. Trans., 1859, p. 417.

Diplumbic triethide	$Pb_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\,?\\C_4H_5\end{array}\right.$
Plumbic oxytriethide	$Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\O\end{array}\right.$
Plumbic chlorotriethide	$Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{array}\right.$
Plumbic triethylosulphate	$Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\SO_4\end{array}\right.$
Plumbic ethide	$Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{array}\right.$

The existence of the first of these bodies cannot be said to be clearly established; but by the action of an alloy of sodium and lead upon iodide of ethyl, a colourless, mobile, volatile liquid is obtained, which, when dissolved in alcohol or ether, and exposed to the air, forms plumbic oxytriethide, a body which is however more readily obtained by the decomposition of the chloride with oxide of silver:

$$\underbrace{Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{array}\right.}_{\text{Plumbic chlorotriethide.}} + AgO = \underbrace{Pb_2\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\O\end{array}\right.}_{\text{Plumbic oxytriethide.}} + AgCl$$

Plumbic ethide is a colourless limpid fluid, soluble in ether, but insoluble in water, and possessing a faint odour. It is not acted upon by oxygen at ordinary temperatures, but chlorine, bromine, and iodine act violently upon it. Plumbic ethide belongs to the class of saturated bodies, and is consequently incapable of forming compounds. When it is treated with hydrochloric acid, hydride of ethyl separates and plumbic chloro-triethide is formed:

$$\underbrace{Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Plumbic ethide.}} + HCl = \underbrace{Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.}_{\text{Plumbic chlorotriethide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}}$$

From plumbic chloro-triethide the sulphates and other salts can be prepared by double decomposition. These salts may also be obtained still more readily from the oxide, which is a crystalline, volatile, pungent body, possessing a powerful alkaline reaction, and attracting carbonic acid from the air.

MERCURIC SERIES.*—This series is confined to bodies of the mercuric type, no organo-mercurous compound having been yet produced. It comprises the following members:

Mercuric methiodide	$Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.$
Mercuric methhydrate	$Hg\left\{\begin{matrix}C_2H_3\\H\,O_2\end{matrix}\right.$
Mercuric methonitrate	$Hg\left\{\begin{matrix}C_2H_3\\N\,O_6\end{matrix}\right.$
Mercuric methide	$Hg\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Mercuric ethiodide	$Hg\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right.$
Mercuric ethohydrate	$Hg\left\{\begin{matrix}C_4H_5\\H\,O_2\end{matrix}\right.$
Mercuric ethonitrate	$Hg\left\{\begin{matrix}C_4H_5\\N\,O_6\end{matrix}\right.$
Mercuric ethide	$Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Mercuric ethylomethide	$Hg\left\{\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right.?$

Mercuric methide and mercuric ethide are colourless, ethereal, volatile liquids, insoluble in water, but insoluble in alcohol and ether, and possessing great stability. They are in a state of maximum saturation, and cannot therefore unite with any other body without the displacement of an equivalent of positive radical. Thus with bromine, mercuric ethide gives bromide of ethyl and mercuric ethylobromide:

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* Frankland, Phil. Trans., 1852, p. 436, and Phil. Trans., 1859, p. 409; Dünhaupt, Ann. Ch. Pharm., xcii, 371; Strecker, Ann. Ch. Pharm., xcii, 57; Buckton, Phil. Trans., 1858, p. 163, and 1859, p. 417.

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + 2Br = \underbrace{Hg\left\{\begin{matrix}C_4H_5\\Br\end{matrix}\right.}_{\text{Mercuric ethylobromide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\Br\end{matrix}\right\}}_{\text{Bromide of ethyl.}}$$

With hydrated sulphuric acid the action is:

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + SO_4H = \underbrace{Hg\left\{\begin{matrix}C_4H_5\\SO_4\end{matrix}\right.}_{\text{Mercuric ethosulphate.}} + \underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}}$$

Mercuric methide possesses the highest specific gravity of any known non-metallic liquid (3·069). Glass consequently floats upon its surface. Brought in contact with mercuric iodide, mercuric methide and mercuric ethide are converted respectively into mercuric methiodide and mercuric ethiodide:

$$\underbrace{Hg\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Mercuric methide.}} + Hg\left\{\begin{matrix}I\\I\end{matrix}\right. = \underbrace{2Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.}_{\text{Mercuric methiodide.}}$$

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + Hg\left\{\begin{matrix}I\\I\end{matrix}\right. = \underbrace{2Hg\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right.}_{\text{Mercuric ethiodide.}}$$

The reaction with mercuric chloride is exactly analogous. The hydrates of mercuric methoxide and mercuric ethoxide are caustic alkaline bases, capable of expelling ammonia from its salts, and behaving in a manner similar to the corresponding uniatomic compounds of tin and lead. The remaining mercury-compounds, which may be considered as derivatives of these two bodies, are represented in the above list by the iodides and nitrates: they generally crystallize very readily, and, with the exception of the haloïd compounds, are soluble in water. When their aqueous solutions are treated with zinc, they are decomposed, the zinc becomes amalgamated, and gaseous hydrides of the positive radicals are evolved. It is highly probable that there are two stages in this reaction, organo-zinc compounds being first formed and then decomposed by contact with water; thus with mercuric methiodide—

$$\underbrace{2Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.}_{\text{Mercuric methiodide.}} + Zn_4 = \underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + 2ZnI + 2Hg$$

and then:

$$\underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + \underbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}_{\text{Water.}} = \underbrace{2\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}}_{\text{Hydride of methyl.}} + 2ZnO$$

This view of the reaction is confirmed by the fact that when zinc acts upon mercuric methiodide at 150° C., zinc-methyl is produced. When one of the above iodides or the corresponding chloride or bromide is treated with an organo-zinc compound, the negative element becomes replaced by the alcohol-radical of the zinc-compound; thus, when mercuric methiodide is treated with zinc-methyl, mercuric methide is produced. And it is believed that by acting upon mercuric ethochloride with zinc-methyl, mercuric ethylomethide is produced:

$$\underbrace{2Hg\left\{\begin{matrix}C_4H_5\\Cl\end{matrix}\right.}_{\text{Mercuric ethochloride.}} + \underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} = \underbrace{2Hg\left\{\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right.}_{\text{Mercuric ethylomethide.}} + 2ZnCl$$

but this body has not yet been obtained in a state of purity; distillation gradually resolves it into mercuric methide and mercuric ethide:

$$\underbrace{2Hg\left\{\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right.}_{\text{Mercuric ethylomethide.}} = \underbrace{Hg\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Mercuric methide.}} + \underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}}$$

ANTIMONY SERIES.*—This important series of organo-metallic bodies contains a greater number and variety of compounds than any other, with the exception of the arsenic series. The remarkable polyatomic character of antimony and arsenic not only renders the possible number of their organo-compounds very large, but the variation in the proportions of the positive and negative molecules gives an extremely wide range to their chemical character, extending, as it does, from highly caustic bases on the one hand to powerful bibasic acids on the other. The following are the principal compounds belonging to this series:

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* Löwig, Ann. Ch. Pharm., lxxv, 315, 327; Landolt, Ann. Ch. Pharm., lxxviii, 91; Buckton, Chem. Soc. Qu. J., xiii, 115; Hofmann, *ibid*, xi, 316.

Trimethylstibine	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$
Antimonic trimethoxide	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\O\\O\end{matrix}\right.$
Antimonic trimethochloride	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\Cl\\Cl\end{matrix}\right.$
Iodide of tetramethylstibonium or antimonic tetramethiodide	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\I\end{matrix}\right.$
Hydrate of tetramethylstibonium or antimonic tetramethylhydrate	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\H\ O_2\end{matrix}\right.$
Antimonic trimethosulphate	$Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\S\ O_4\\S\ O_4\end{matrix}\right.$
Triethylstibine	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$
Antimonic triethoxide	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.$

Antimonic triethochloride	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.$
Iodide of tetrethylstibonium or antimonic tetramethiodide	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.$
Iodide of methylo-triethylstibonium or antimonic triethomethiodide	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_2H_3\\I\end{matrix}\right.$
Hydrate of tetrethylstibonium or antimonic tetrethylhydrate	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\H\,O_2\end{matrix}\right.$
Antimonic triethosulphate	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\S\,O_4\\S\,O_4\end{matrix}\right.$
Sulphate of tetrethylstibonium or antimonic tetrethylsulphate	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\S\,O_4\end{matrix}\right.$
Antimonic triethantimonite	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\SbO_4\\SbO_4\end{matrix}\right.$
Antimonic triethoxiodide	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\\I\end{matrix}\right.$
Triamylstibine	$Sb\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.$

Antimonic triamylchloride $\quad Sb\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\\Cl\\Cl\end{matrix}\right.$

Antimonic triamylnitrate $\quad Sb\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\\N\ O_6\\N\ O_6\end{matrix}\right.$

It is remarkable that we have as yet no decisive evidence in this series, of the existence of a compound corresponding to cacodyl. It is true that such a body has been described under the name of *stibbiamyl,* but subsequent experiments have failed to confirm its existence. Amongst organo-antimony compounds, therefore, the most simple form is $Sb\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.$. Bodies of this form are the analogues of ammonia, and need not be here described, since their history, and also that of bodies having the form $Sb\left\{\begin{matrix}R+\\R+\\R+\\R+\\R-\end{matrix}\right.$ will be found in a discourse upon "Ammonia and its Derivatives," delivered to this Society, June 17th, 1858, by Dr. Hofmann.*

The only bodies, therefore, of this series requiring notice here are those of the form $Sb\left\{\begin{matrix}R+\\R+\\R+,\\R-\\R-\end{matrix}\right.$ and their derivatives. When the two atoms of R— are oxygen, these compounds constitute what may be termed biacid antimony bases. They are formed either by the direct union of the stibamines $\left(Sb\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.\right)$ with oxygen.

$$Sb\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right. \quad + \quad O_2 \quad = \quad Sb\left\{\begin{matrix}R+\\R+\\R+\\O\\O\end{matrix}\right.$$

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* See vol. xi, p. 252, of this Journal.

or by the decomposition of the corresponding haloïd compounds by means of potash: thus—

$$\mathrm{Sb}\left\{\begin{array}{l}\mathrm{R}\\ \mathrm{R}\\ \mathrm{R}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. + 2\mathrm{KO} = \mathrm{Sb}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\\ \mathrm{O}\\ \mathrm{O}\end{array}\right. + 2\mathrm{KCl}$$

The stibamines, although in other respects the perfect analogues of the nitramines, here evidently exhibit a much more highly positive character, uniting with oxygen so energetically as to be spontaneously inflammable in the lower portion of the series.

The biacid antimony bases are colourless, transparent, amorphous, and tenacious bodies; the ethyl base is easily soluble in water and alcohol, but somewhat less soluble in ether. They possess a bitter taste, are non-volatile, and do not suffer any change when exposed to the air. Treated with potassium they are reduced to stibamines:

$$\mathrm{Sb}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\\ \mathrm{O}\\ \mathrm{O}\end{array}\right. + 2\mathrm{K} = \mathrm{Sb}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\end{array}\right. + 2\mathrm{KO}$$

Fuming nitric acid decomposes the biacid bases with ignition; but when they are treated with dilute nitric or other acid, the respective biacid salts are produced. The oxysalts are soluble in water or alcohol; most of them crystallise without much difficulty, as do also the antimonic biniodides; but antimonic triethobromide and triethochloride are liquids not volatile without decomposition, insoluble in water, but soluble in alcohol and ether.

The existence of antimonic triethoxiodide has been recently proved by **Strecker**. It had previously been regarded by **Merck** as a protoiodide of stibethine $(\mathrm{Sb}(\mathrm{C_4H_5})_3\mathrm{I})$.

ARSENIC SERIES.*—This series is perhaps the most important and interesting amongst organo-metallic bodies; it contains the first discovered organo-metal, cacodyl, the classical investigation of which by Bunsen not only imparts a completeness to our knowledge of this series, but has afforded the clue to the successful interpretation of many phenomena met with in other analogous families. It will be convenient to divide its very numerous members into three groups.

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* **Cadet** (1760), Mém. de Math. et Phys. de Savants étrang., iii, 633; **Thénard**, Ann. Ch. lii, 54; **Bunsen**, Ann. Ch. Pharm., xxiv, 27; xxvii, 1; xlii, 14; xlvi, 1; **Frankland**, Ch. Soc. Qu. J., ii, 299; **Cahours et Riche**, Compt. rend., xxxvi, 1001; **Landolt**, Ann. Ch. Pharm., lxxxix, 301; **Hofmann**, Chem. Soc. Qu. J., xi, 316. **Baeyr**, Ann. Ch. Pharm. cvii, 257; cv. 265.

A. Organo-arsenical compounds of the type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\end{matrix}\right.$

B. Organo-arsenical compounds of the type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\\\mathrm{R}\end{matrix}\right.$

C. Organo-arsenical compounds of the type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\\\mathrm{R}\\\mathrm{R}\\\mathrm{R}\end{matrix}\right.$

All arsenical compounds permit of being arranged under these three types. The following are the principal bodies already investigated:

A. Organo-arsenical Compounds of the Type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\end{matrix}\right.$

Cacodyl	$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Ethylic cacodyl	$\mathrm{As}\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Propylic cacodyl	$\mathrm{As}\left\{\begin{matrix}C_6H_7\\C_6H_7\end{matrix}\right.?$
Butylic cacodyl	$\mathrm{As}\left\{\begin{matrix}C_8H_9\\C_8H_9\end{matrix}\right.?$

B. Organo-arsenical Compounds of the Type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\\\mathrm{R}\end{matrix}\right.$

Oxide of cacodyl	$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right.$
Sulphide of cacodyl	$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\S\end{matrix}\right.$
Chloride of cacodyl	$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\end{matrix}\right.$

Chloride of cacoplatyl $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_2H_3}\\ \mathrm{C_2Pt''H}\\ \mathrm{Cl}\end{array}\right.$

Arsenious dioxymethide $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_2H_3}\\ \mathrm{O}\\ \mathrm{O}\end{array}\right.$

Arsenious disulphomethide $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_2H_3}\\ \mathrm{S}\\ \mathrm{S}\end{array}\right.$

Arsenious dichloromethide $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_2H_3}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.$

Trimethylarsine $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_2H_3}\\ \mathrm{C_2H_3}\\ \mathrm{C_2H_3}\end{array}\right.$

Arsenious diethiodide $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_4H_5}\\ \mathrm{C_4H_5}\\ \mathrm{I}\end{array}\right.$

Triethylarsine $\mathrm{As}\left\{\begin{array}{c}\mathrm{C_4H_5}\\ \mathrm{C_4H_5}\\ \mathrm{C_4H_5}\end{array}\right.$

C. Organo-arsenical Compounds of the Type $\mathrm{As}\left\{\begin{array}{l}\mathrm{R}\\ \mathrm{R}\\ \mathrm{R}\\ \mathrm{R}\\ \mathrm{R}\end{array}\right.$

This group may be conveniently divided into four families or sub-types, viz.:

a. Bodies of the form $\mathrm{As}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}-\\ \mathrm{R}-,\\ \mathrm{R}-\\ \mathrm{R}-\end{array}\right.$ and their derivatives.

b. Bodies of the form $\mathrm{As}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}-,\\ \mathrm{R}-\\ \mathrm{R}-\end{array}\right.$ and their derivatives.

c. Bodies of the form $\mathrm{As}\left\{\begin{array}{l}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+,\\ \mathrm{R}-\\ \mathrm{R}-\end{array}\right.$ and their derivatives.

d. Bodies of the form $\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}-\end{matrix}\right.$

a. Sub-type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}-\\\mathrm{R}-\\\mathrm{R}-\\\mathrm{R}-\end{matrix}\right.$

Monomethylarsenic acid $\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right.$

Monomethylarseniates $\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\MO_2\\MO_2\end{matrix}\right.$

Arsenic dioxydichlormethide $\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\Cl\\Cl\end{matrix}\right.$

Arsenic tetrachlormethide $\mathrm{As}\left\{\begin{matrix}C_2H_3\\Cl\\Cl\\Cl\\Cl\end{matrix}\right.$

b. Sub-type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}-\\\mathrm{R}-\\\mathrm{R}-\end{matrix}\right.$

Cacodylic Acid $\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.$

Cacodylates $\mathrm{As}\left\{\begin{array}{c}C_2H_3\\C_2H_3\\O\\O\\MO_2\end{array}\right.$

Sulphocacodylic acid $\mathrm{As}\left\{\begin{array}{c}C_2H_3\\C_2H_3\\S\\S\\S\end{array}\right.$

Sulphocacodylates $\mathrm{As}\left\{\begin{array}{c}C_2H_3\\C_2H_3.\\S\\S\\MS_2\end{array}\right.$

Terchloride of cacodyl $\mathrm{As}\left\{\begin{array}{c}C_2H_3\\C_2H_3\\Cl\\Cl\\Cl\end{array}\right.$

Ethyl-cacodylic acid $\mathrm{As}\left\{\begin{array}{c}C_4H_5\\C_4H_5\\O\\O\\O\end{array}\right.$

Ethyl-cacodylates $\mathrm{As}\left\{\begin{array}{c}C_4H_5\\C_4H_5\\O\\O\\MO_2\end{array}\right.$

c. Sub-type $\mathrm{As}\left\{\begin{array}{l}R+\\R+\\R+\\R-\\R-\end{array}\right.$

Arsenic triethoxide $\mathrm{As}\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{array}\right.$

Arsenic triethosulphate
$$As\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\S\ O_4\\S\ O_4\end{array}\right.$$

Arsenic triethosulphide
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\S\\S\end{array}\right.$$

Arsenic triethochloride
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\Cl\\Cl\end{array}\right.$$

d. Bodies of the form $As\left\{\begin{array}{l}R+\\R+\\R+\\R+\\R-\end{array}\right.$

Oxide of tetramethylarsonium
or arsenic tetramethoxide
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\O\end{array}\right.$$

Sulphate of tetramethylarsonium
or arsenic tetramethylsulphate
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\SO_4\end{array}\right.$$

Iodide of tetramethylarsonium
or arsenic tetramethiodide
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\I\end{array}\right.$$

Oxide of dimethyl-diethylarsonium
or arsenic dimethyl-diethyloxide
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\\O\end{array}\right.$$

Iodide of dimethyl-diethylarsonium or arsenic dimethyl-diethyliodide	$\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\\I\end{cases}$
Nitrate of dimethyl-diethylarsonium or arsenic dimethyl-diethylnitrate	$\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\\N\,O_6\end{cases}$
Oxide of tetrethylarsonium or arsenic tetrethoxide	$\mathrm{As}\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\O\end{cases}$
Sulphate of tetrethylarsonium or arsenic tetrethylsulphate	$\mathrm{As}\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\S\,O_4\end{cases}$
Chloride of tetrethylarsonium or arsenic tetrethylchloride	$\mathrm{As}\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{cases}$
Iodide of dimethyl-diamylarsonium or arsenic diamyliodide	$\mathrm{As}\begin{cases}C_2\,H_3\\C_2\,H_3\\C_{10}H_{11}\\C_{10}H_{11}\\I\end{cases}$

The organo-arsenical compounds belonging to the type $\mathrm{As}\begin{cases}R\\R\end{cases}$ contain only positive radicals. They are volatile poisonous liquids, insoluble in water, but very soluble in alcohol and ether, and possessing an insupportable odour. The lower members of the family are spontaneously inflammable, whilst the higher ones also rapidly oxidise in air. They unite with negative elements with great energy, manifesting in their combinations either a uniatomic or a teratomic character, and producing bodies either of the form $\mathrm{As}\begin{cases}R+\\R+\\R-\end{cases}$ or $\mathrm{As}\begin{cases}R+\\R+\\R-.\\R-\\R-\end{cases}$ Thus cacodyl forms with chlorine, chloride of cacodyl and terchloride of cacodyl.

$$\underset{\text{Cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\end{cases}}} + \mathrm{Cl} = \underset{\text{Chloride of cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\\\mathrm{Cl}\end{cases}}}$$

$$\underset{\text{Cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\end{cases}}} + \mathrm{Cl}_3 = \underset{\text{Terchloride of cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{cases}}}$$

Methylic cacodyl boils at 170° C., and ethylic cacodyl between 185° and 190° C.

Heated to 400° C., cacodyl splits up into metallic arsenic, hydride of methyl, and olefiant gas:

$$\underset{\text{Cacodyl.}}{\underline{2\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\end{cases}}} = \mathrm{As}_2 + \underset{\text{Hydride of methyl.}}{\underline{2\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}}} + \underset{\text{Olefiant gas.}}{\underline{C_4H_4}}$$

Bodies of this type can be regenerated by reducing agents from many of their uniatomic compounds; thus chloride of cacodyl and metallic zinc give cacodyl and chloride of zinc:

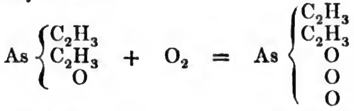
$$\underset{\text{Chloride of cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\\\mathrm{Cl}\end{cases}}} + \mathrm{Zn} = \underset{\text{Cacodyl.}}{\underline{\mathrm{As}\begin{cases}C_2H_3\\C_2H_3\end{cases}}} + \mathrm{ZnCl}$$

Organo-arsenical compounds of the type $\mathrm{As}\begin{cases}R\\R\\R\end{cases}$ are of three forms, viz.:

$$(1)\ \mathrm{As}\begin{cases}R+\\R+\\R+\end{cases} \qquad (2)\ \mathrm{As}\begin{cases}R+\\R+\\R-\end{cases} \qquad (3)\ \mathrm{As}\begin{cases}R+\\R-\\R-\end{cases}$$

Those belonging to the first are termed *arsines*, and are the analogues of ammonia; but, like the corresponding antimony compounds, in addition to their alkaloid function, they have the power of combining with two negative atoms, forming bodies of the sub-type $\mathrm{As}\begin{cases}R+\\R+\\R+\\R-\\R-\end{cases}$. Thus triethylarsine combines with oxygen to form arsenic dioxytriethide. The lower members of the type possess this property to such an extent as to render them spontaneously imflammable in air.

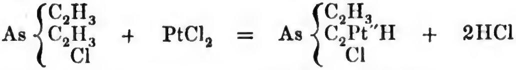
Compounds belonging to the second of the above forms are produced by the direct combination of the cacodyls with negative elements, the oxides are bases of comparatively feeble power, slowly combining with two additional equivalents of oxygen, to form acids. Thus oxide of cacodyl, by exposure to air, slowly passes into cacodylic acid:



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right. + O_2 = \mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.$$

Oxide of cacodyl. Cacodylic acid.

The chlorine, bromine, and iodine compounds of the form we are now considering are volatile neutral bodies, which may be regarded as the haloïd salts of cacodyl. Heated in contact with bichloride of platinum, the chloride of cacodyl presents an interesting re-action; two equivalents of hydrogen in the cacodyl become replaced by a biatomic molecule of platinum, producing chloride of cacoplatyl.

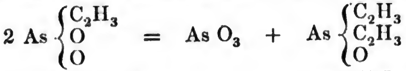


$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\end{matrix}\right. + PtCl_2 = \mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2Pt''H\\Cl\end{matrix}\right. + 2HCl$$

Chloride of cacodyl. Chloride of cacoplatyl.

Cacoplatyl forms a series of compounds analogous to those of cacodyl.

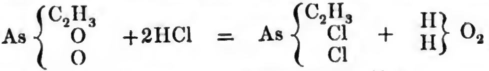
The only compounds of the third form yet known belong to the methylic group. Arsenious dioxymethide is a crystalline body of a neutral character, soluble in water, alcohol, and ether, unchanged by exposure to air, but transformed by distillation with hydrate of potash into arsenious acid and oxide of cacodyl:



$$2\,\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right. = \mathrm{As}\,O_3 + \mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right.$$

Arsenious dioxymethide. Oxide of cacodyl.

Hydrochloric acid converts it into arsenious dichlormethide:



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right. + 2HCl = \mathrm{As}\left\{\begin{matrix}C_2H_3\\Cl\\Cl\end{matrix}\right. + \left.\begin{matrix}H\\H\end{matrix}\right\}O_2$$

Arsenious dioxymethide. Arsenious dichlormethide.

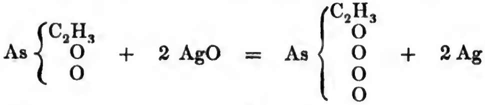
Hydrobromic and hydriodic acids produce a perfectly analogous change, whilst sulphuretted hydrogen tranforms it into arsenious disulphomethide. The chloric compound can also be formed by heating arsenic trichlormethide to 50° C.

$$\underset{\text{Arsenic trichlormethide.}}{\underline{\mathrm{As}\left\{\begin{array}{l}\mathrm{C_2H_3}\\\mathrm{C_2H_3}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right.}} = \underset{\text{Arsenious dichlormethide.}}{\underline{\mathrm{As}\left\{\begin{array}{l}\mathrm{C_2H_3}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right.}} + \underset{\text{Chloride of methyl.}}{\underline{\left.\begin{array}{l}\mathrm{C_2H_3}\\\mathrm{Cl}\end{array}\right\}}}$$

The chlorine, bromine, and iodine compounds are neutral bodies of considerable stability; the two former are liquid, the latter solid and crystalline. By the action of chlorine or oxidising agents, they are transformed into bodies of the form $\mathrm{As}\left\{\begin{array}{l}R\ +\\R\ -\\R\ -\\R\ -\\R\ -\end{array}\right.$

Organo-arsenical compounds have been more thoroughly investigated in the direction of the type $\mathrm{As}\left\{\begin{array}{l}R\\R\\R\\R\\R\end{array}\right.$ than in any other; consequently we find these bodies rather numerously represented, especially under the subtype $\mathrm{As}\left\{\begin{array}{l}R\ +\\R\ +\\R\ +\\R\ +\\R\ -\end{array}\right.$. As the latter bodies, however, are the strict analogues of the compounds of ammonium, their chemical relations will be found fully described in Dr. Hofmann's discourse before alluded to,

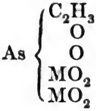
Sub-type $\mathrm{As}\left\{\begin{array}{l}R\ +\\R\ -\\R\ -\\R\ -\\R\ -\end{array}\right.$ has only yet been explored in the methylic group. The oxygen-compound constitutes anhydrous monomethylarsenic acid, a direct derivative from arsenious dioxymethide:



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right. + 2\,AgO = \mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right. + 2\,Ag$$

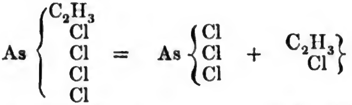
Arsenious dioxymethide. Monomethylarsenic acid.

This acid is bibasic, forming stable and well defined crystallisable salts, the formulæ of which are represented by the general expression



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\MO_2\\MO_2\end{matrix}\right.$$

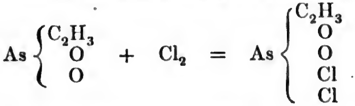
The chlorine compound is exceedingly unstable; it may however be formed at —10°C., but is transformed at 0°C. into arsenious chloride and chloride of methyl:



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\Cl\\Cl\\Cl\\Cl\end{matrix}\right. = \mathrm{As}\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. + \left.\begin{matrix}C_2H_3\\Cl\end{matrix}\right\}$$

Arsenic tetrachlormethide. Chloride of methyl.

Arsenic dioxydichlormethide is a somewhat more stable body formed by the direct union of chlorine with arsenious dioxymethide.



$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right. + Cl_2 = \mathrm{As}\left\{\begin{matrix}C_2H_3\\O\\O\\Cl\\Cl\end{matrix}\right.$$

Arsenious dioxymethide. Arsenic dioxydichlormethide.

Nevertheless, even this compound readily decomposes, with evolution of chloride of methyl.

Sub-type $\mathrm{As}\left\{\begin{matrix}R\ +\\R\ +\\R\ -\\R\ -\\R\ -\end{matrix}\right.$ The oxygen-compounds are feeble monobasic acids of which cacodylic acid may be regarded as the representative. They are derived from the bodies $\mathrm{As}\left\{\begin{matrix}R\ +\\R\ +\\O\end{matrix}\right.$ by direct oxidation as already described. Cacodylic acid is remarkable for its stability; neither fuming nitric acid nor a mixture of sulphuric; and chromic acids attack it, even at the boiling point, and it may be heated to 200° C. without alteration. Although it is soluble in water and contains upward of 54 per cent. of arsenic, yet it is not in the least poisonous. Several agents reduce cacodylic acid to the arsenious or even to the diatomic form. Thus phosphorous acid transforms it into cacodyl:

$$\underbrace{2\,As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\O\\O\\O\end{array}\right.}_{\text{Cacodylic acid.}} \quad + \quad 3\,P\left\{\begin{array}{c}O\\O\\O\end{array}\right. \quad = \quad \underbrace{2\,As\left\{\begin{array}{c}C_2H_3\\C_2H_3\end{array}\right.}_{\text{Cacodyl.}} \quad + \quad 3\,PO_5$$

Zinc also produces the same result. Hydriodic acid gas converts cacodylic acid into arsenious dimethiodide:

$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\O\\O\\O\end{array}\right. \quad + \quad 3\,HI \quad = \quad As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\I\end{array}\right. \quad + \quad I_2 \quad + \quad 3\,HO$$

The acid character of this body is so slightly marked as to render it capable of forming compounds in which it appears to play the part of a base. Thus with hydrofluoric, hydrochloric and hydrobromic acids, it forms the following compounds:

Hydrofluate of cacodylic acid] $As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\F\end{array}\right.$

Hydrochlorate of cacodylic acid $As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\Cl\end{array}\right.$

Hydrobromate of cacodylic acid $As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\Br\end{array}\right.$

The hydrobromate reacts perfectly neutral. The cacodylates have the formula:

$$As \left\{ \begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ O \\ MO_2 \end{array} \right.$$

Sulphocacodylic acid has not yet been isolated, but its salts present the same relations to those of cacodylic acid, as salts of sulphur-acids generally bear to those of oxyacids. Their formula is

$$As \left\{ \begin{array}{c} C_2H_3 \\ C_2H_3 \\ S \\ S \\ MS_2 \end{array} \right.$$

Sub-type $As \left\{ \begin{array}{ll} R & + \\ R & + \\ R & + \\ R & - \\ R & - \end{array} \right.$ has hitherto been very little explored, so far as it is known, but its members bear so close a resemblance to their analogues in the antimony-series, as to require no further notice.

TELLURIUM SERIES.* The close relations of tellurium to sulphur and selenium place the bodies of this series in the same position with regard to the sulphides and selenides of the alcohol-radicals as the antimony and arsenic series stand in relation to the corresponding compounds of phosphorus and nitrogen.

The following bodies belonging to this series are known:

Tellurium methyl	$Te_2 \left\{ \begin{array}{c} C_2H_3 \\ C_2H_3 \end{array} \right.$
Tellurous dimethoxide	$Te_2 \left\{ \begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ O \end{array} \right.$
Tellurous methoxychloride	$Te_2 \left\{ \begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ Cl \end{array} \right.$

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* Wöhler, Ann. Ch. Pharm., xxxv, 112, lxxxiv, 69; Mallet, Ann. Ch. Pharm., lxxix, 223; Wöhler and Dean, Ann. Ch. Pharm., xciii, 233.

Tellurous dimethiodide	$Te_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\I\\I\end{matrix}\right.$
Tellurium-ethyl	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Tellurous diethoxide	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.$
Tellurous diethosulphide	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\S\\S\end{matrix}\right.$
Acid tellurous diethosulphate	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\HO_2\\SO_4\end{matrix}\right.$
Tellurous diethochloride	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.$
Tellurous diethoxychloride	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\O\end{matrix}\right.$
Tellurous diethiodide	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.$
Tellurium-amyl	$Te_2\left\{\begin{matrix}C_{10}H_{11}?\\C_{10}H_{11}\end{matrix}\right.$

The compounds of the alcohol-radicals with tellurium are volatile liquids of most unbearable odour. They oxidise readily in contact with air, forming the respective oxides. Tellurium-amyl has not yet been obtained in a state of purity.

The oxides of these bodies are powerful bases, expelling ammonia from its salts, and attracting carbonic acid from the air. They form salts of considerable stability, which, as well as the oxides themselves, yield the original organo-tellurium compounds when treated with sulphurous acid:

$$\underbrace{Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.}_{\text{Tellurous diethoxide.}} + S_2O_4 = \underbrace{Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Tellurium ethyl.}} + S_2O_6$$

Constitution, and Theoretical Importance of Organo-metallic Bodies.

In the year 1852*, at a time when comparatively little progress had been made in the investigation of organo-metallic bodies, I ventured to propose a view of their constitution which further research has completely confirmed. According to this view, the organo-metallic bodies are constructed upon the types of the inorganic chlorides, sulphides, oxides, &c., of the respective metals which they contain, the chlorine, oxygen, sulphur, &c., being replaced in equivalent proportion and step by step by the alcohol-radicals.

A reference to the formulæ of organo-potassium, sodium, magnesium, zinc, and cadmium compounds given above, shows that they are all formed upon the models of the protochlorides of these metals; the general type being

$$M_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$$

In like manner organo-aluminium compounds are formed upon the type of the sesquichloride of that metal:

$$Al_2\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$$

Organo-tin compounds are represented by the three chlorides of tin:

$$Sn_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$$

The compounds of the bismuth-series are represented by the terchloride of bismuth and by bismuthic acid:

$$Bi\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. \qquad Bi\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right.$$

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* Phil. Trans. for 1852, p. 438.

Organo-lead compounds are arranged under the types of sesquioxide and peroxide of lead :

$$\mathrm{Pb_2}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\right. \qquad\qquad \mathrm{Pb_2}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\right.$$

The mercury-series are all moulded upon the type of the bichloride :

$$\mathrm{Hg}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.$$

The *arsenic* and *antimony* series have for their types the following inorganic compounds :

$$\mathrm{As}\left\{\begin{matrix}\mathrm{S}\\ \mathrm{S}\end{matrix}\right. , \quad \mathrm{As}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. , \quad \mathrm{As}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\right. , \quad \mathrm{Sb}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. , \quad \mathrm{Sb}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.$$

The inorganic models for the tellurium series are chloride of tellurium and tellurous acid :

$$\mathrm{Te_2}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. \qquad\qquad \mathrm{Te_2}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\right.$$

Occasionally an abnormal compound has made its appearance, such as ethostibilic acid ($Sb\ (C_4\ H_5)\ 0_5$) or iodide of triethylstibine ($Sb\ (C_4\ H_5)_3\ J$); but further research has invariably demonstrated the incorrectness of such formulæ and the conformity of the bodies with the normal inorganic types. Indeed this law may now be regarded as sufficiently established to be applicable to the control of the formulæ of new organo-metallic bodies.

From the point of view thus afforded, it is interesting to watch the effect of the substitution in metallic compounds, of basylous or positive for chlorous or negative radicals. Such a substitution affords striking evidence of the dependence of the chemical character of a compound upon that of each individual constituent. The highly polyatomic metals, such as arsenic and antimony, exhibit this dependence in the most conclusive manner. Thus tribasic arsenic acid, by the substitution of an equivalent of methyl for oxygen, yields the bibasic monomethyl-arsenic acid, a well defined acid of considerable energy, though inferior in chlorous power to arsenic acid. The like substitution of a second equivalent of methyl for oxygen, reduces the chlorous character of the body to the comparatively feeble condition in which we find it in cacodylic acid, which is incapable of forming an ammonia-salt. A similar substitution for the third time, overpowers the acid attribute of the compound altogether, and we now have a feeble biacid base, the arsenic dioxymethide, which again, by the exchange of a fourth atom of oxygen for methyl, is transformed into the oxide of tetramethylarsonium, a base of such energy, as to be comparable with the caustic alkalies themselves.

The behaviour of the organo-metallic bodies teaches a doctrine which affects chemical compounds in general, and which may be called the doctrine of atomic saturation; each element is capable of combining with a certain limited number of atoms; and this number can never be exceeded, although the energy of its affinities may have been increased by combination up to this point. Thus zinc appears to attain its atomic saturation by uniting with only one atom of another body; in other words, it is uniatomic, consequently the zinc compounds of the alcohol-radicals, notwithstanding their intense affinities, are incapable of direct union with other bodies. The action of chlorous elements upon them is apparently one of substitution not of combination. Polyatomic metals exhibit the same phenomenon. A double atom of tin cannot combine with more than four atoms; a single atom of arsenic or antimony with more than five atoms of other bodies; but in the combinations of polyatomic metals, we frequently notice from the lowest to the highest compound one or more intermediate points of exalted stability; thus antimony has a teratomic stage of comparative stability; nitrogen, phosphorus, and arsenic, whilst exhibiting a similar teratomic stage, have also a biatomic one, though of greatly inferior stability; whilst the existence of protoxide of nitrogen renders it more than probable that nitrogen has a third and uniatomic stage.

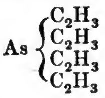
In bodies possessing at least one stage of stability below saturation, and in which all the atoms united with the polyatomic element are of the same kind, the stage of maximum stability is very rarely that of saturation. Thus in nitrogen, arsenic, and bismuth compounds of the kind just mentioned, the stage of maximum stability is decidedly the teratomic one; in antimonial compounds of a similar nature the teratomic is also, though less decidedly, the stage of maximum stability, whilst in phosphorous compounds the points of maximum stability and of saturation generally coincide. When, however, the atoms united with the polyatomic element are not of the same kind, then the stage of maximum stability usually coincides with that of saturation. Thus the binoxide or bichloride of triethylarsine or triethylstibine are more stable than triethylarsine, or triethylstibine themselves; but this pentatomic stability reaches its climax in arsonium, stibonium, and phosphonium compounds, as it does also in the corresponding compounds of nitrogen, although the latter element exhibits a much stronger tendency towards universal teratomic stability than its chemical associates.

In polyatomic organo-metallic bodies, it is remarkable that, with few exceptions, the positive hydrocarbons hold their position much more tenaciously than the associated negative constituents; and we thus frequently find the former accompanying the metal through a vast number of compounds. Hence the group formed by the metal and positive hydrocarbons has come to be regarded as a compound radical. Thus cacodyl is conceived to be the radical of the whole series of cacodyl compounds. But however great may be the convenience of this mode of viewing organo-metallic compounds, and the same mode has notoriously been extended to nearly all organic bodies, it must not be forgotten that it is a purely artificial distinction, which has no real existence, either in the case of organo-metallic bodies, or, as I shall endeavour to show, in that of organic bodies in general.

A close examination of the habits of the so-called organo-metallic radicals shows clearly, that their atomic power depends upon their position with regard to the stages of stability and maximum saturation; thus they are uniatomic when the number of positive groups is one less than that required to reach either the maximum saturation of the metal, or a lower stage of stability. Cacodyl and tetramethyl-arsonium, for instance, are uniatomic radicals, because they are respectively one atom short of the stage of stability, and of maximum saturation:

Uniatomic stage.	Stage of stability.
$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$	$\mathrm{As}\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\end{matrix}\right.$
Cacodyl.	Chloride of cacodyl.

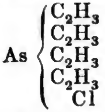
Uniatomic stage.



$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$$

Tetramethylarsonium.

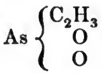
Stage of maximum saturation.



$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\Cl\end{matrix}\right.$$

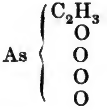
Chloride of tetramethylarsonium.

It is obvious that a compound radical, the number of whose positive atoms is below that of a stage of stability, can have a double atomic character. Thus cacodyl is sometimes uniatomic, as in oxide of cacodyl; and sometimes teratomic, as in cacodylic acid. Again arsenio-monomethyl (AsC_2H_3) is biatomic in arsenious dioxymethide:



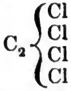
$$As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.$$

and quadratomic in monomethylarsenic acid:



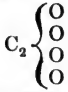
$$As\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right.$$

If these views of the constitution and character of organo-metallic bodies and their compounds be correct, their application to the organic compounds of carbon becomes inevitable. Regarded from this point of view, the double atom of carbon, like that of tin, is quadratomic in perchloride of carbon and carbonic acid:



$$C_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$$

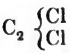
Perchloride of carbon.



$$C_2\left\{\begin{matrix}O\\O\\O\\O\end{matrix}\right.$$

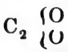
Carbonic acid.

and biatomic in protochloride of carbon and carbonic oxide:



$$C_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$$

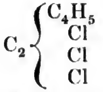
Protochloride of carbon.



$$C_2\left\{\begin{matrix}O\\O\end{matrix}\right.$$

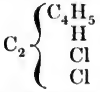
Carbonic oxide.

In other words, the quadratomic stage in carbon-compounds is the stage of maximum saturation, whilst the biatomic stage is one of exalted stability. If we substitute an atom of chlorine in perchloride of carbon by one of ethyl, we produce a body having the formula of trichlorhydrin:



$$C_2\left\{\begin{matrix}C_4H_5\\ Cl\\ Cl\\ Cl\end{matrix}\right.$$

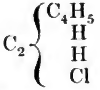
If now a second atom of chlorine be substituted by one of hydrogen, we have a body exhibiting the composition of bichloride of propylene:



$$C_2\left\{\begin{matrix}C_4H_5\\ H\\ Cl\\ Cl\end{matrix}\right.$$

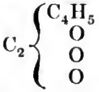
This view of the constitution of bichloride of propylene renders its relations to allyl and glycerin compounds at once simple and intelligible.

The substitution of a third atom of hydrogen gives the formula of chloride of propyl:



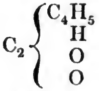
$$C_2\left\{\begin{matrix}C_4H_5\\ H\\ H\\ Cl\end{matrix}\right.$$

whilst the substitution of the last atom of chlorine by hydrogen yields hydride of propyl, and its replacement by ethyl yields the so-called double radical ethylpropyl. It still remains for experiment to produce these bodies from perchloride of carbon, and to show that they are identical with the known compounds possessing the same percentage composition.* If, however, we turn to the oxygen-compounds of carbon, we are not entirely without experimental evidence of the correctness of this view; since one atom of oxygen in carbonic acid has been replaced by ethyl, with production of the body theoretically indicated, namely propionic acid:



$$C_2\left\{\begin{matrix}C_4H_5\\ O\\ O\\ O\end{matrix}\right.$$

Could a second atom of oxygen be substituted by hydrogen, we ought to produce propionic aldehyde:



$$C_2\left\{\begin{matrix}C_4H_5\\ H\\ O\\ O\end{matrix}\right.$$

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* Such experiments are in progress, but are not sufficiently advanced to be here quoted.

The replacement of a third atom of oxygen by hydrogen would then yield propylic ether:

$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad H\\ \quad H\\ \quad O\end{array}\right.$$

whilst the replacement of the last atom of oxygen by hydrogen should give rise to hydride of propyl, and by uniatomic peroxide of hydrogen, to propylic alcohol:

$$\underset{\text{Hydride of propyl.}}{\underline{C_2\left\{\begin{array}{l}C_4H_5\\ \quad H\\ \quad H\\ \quad H\end{array}\right.}}\qquad\qquad \underset{\text{Propylic alcohol.}}{\underline{C_2\left\{\begin{array}{l}C_4H_5\\ \quad H\\ \quad H\\ \quad HO_2\end{array}\right.}}$$

The glycols, are also constructed upon the carbonic acid type:

$$\underset{\text{Glycol.}}{\underline{C_2\left\{\begin{array}{l}C_2H_3\\ \quad H\\ \quad HO_2\\ \quad HO_2\end{array}\right.}}$$

and to the same type belongs also the teracid alcohol, glycerin.

$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad HO_2\\ \quad HO_2\\ \quad HO_2\end{array}\right.$$

Under the influence of iodide of phosphorus, glycerin yields iodide of allyl:

$$\underset{\text{Glycerin.}}{\underline{C_2\left\{\begin{array}{l}C_4H_5\\ \quad HO_2\\ \quad HO_2\\ \quad HO_2\end{array}\right.}} + P\left\{\begin{array}{l}I\\I\\I\end{array}\right. = \underset{\text{Iodide of allyl.}}{\underline{C_2\left\{\begin{array}{l}C_4H_5\\ \quad I\end{array}\right.}} + \underset{\text{Phosphoric acid.}}{\underline{P\left\{\begin{array}{l}O\\O\\HO_2\\HO_2\\HO_2\end{array}\right.}} + I_2$$

Here we have a reduction from the carbonic acid to the carbonic oxide type, of precisely the same nature as that which occurs when cacodylic acid is reduced to oxide of cacodyl. Allylic compounds are therefore constructed upon the carbonic oxide type.

$$C_2\left\{\begin{matrix}O\\O\end{matrix}\right. \quad , \quad C_2\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right. \quad , \quad C_2\left\{\begin{matrix}C_4H_5\\HO_2\end{matrix}\right.$$

Carbonic oxide. Iodide of allyl. Allylic alcohol.

It would be easy greatly to extend this view of the constitution of organic carbon compounds; but the above examples are sufficient to indicate its general application somewhat more fully than I have previously done,* and more than this is not desirable until the hypothesis has been further supported by experimental results.

In conclusion, it is evident that this is only one mode of applying to organic compounds the law of chemical combination which I have endeavoured to deduce from the constitution and behaviour of organo-metallic bodies. Its application ought to be, and will be found to be, equally truthful in referring organic compounds containing hydrogen, oxygen, or nitrogen, to the inorganic typical compounds of each of these elements. Thus, for example, we can represent alcohol:

1st, as derived from carbonic acid:

$$C_2\left\{\begin{matrix}C_2H_3\\H\\H\\HO_2\end{matrix}\right.$$

2nd, as derived from teroxide of hydrogen:

$$H\left\{\begin{matrix}C_4H_5\\O\\O\end{matrix}\right. = H\left\{\begin{matrix}C_2\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.\\O\\O\end{matrix}\right.$$

3rd, as derived from water:

$$O_2\left\{\begin{matrix}C_4H_5\\H\end{matrix}\right. = O_2\left\{\begin{matrix}C_2\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.\\H\end{matrix}\right. .$$

In like manner, nitrogen compounds and their analogues, whilst derived from typical inorganic compounds of nitrogen, are also true derivatives from the carbon types. Thus trimethylamine is correctly written as a derivative from carbonic acid:

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* Ann. Ch. Pharm., ci, 260; Proc. of Royal Inst. of Great Britain for 1858. It is highly remarkable that more than thirteen years ago, when such analogies were of the most obscure kind, the quick perception of Liebig led him to point out analogous relations between carbonic acid, alcohol, formic acid, and marsh gas. See Ann. Ch. Pharm., lviii, 335.)

$$C_2\left\{\begin{matrix}N\,(C_2H_3)_2\\H\\H\\H\end{matrix}\right.$$

Each of these modes of notation is equally correct; but I conceive that a large number of those organic bodies, which are usually formulated in accordance with the hydrogen, water, and hydrochloric acid models, would be much more usefully expressed upon the carbonic acid and carbonic oxide types. The formulation of organic compounds is not a matter of indifference, even to the chemical investigator; and hence every mode of expression founded upon broad chemical relations ought to have the preference over more purely artificial methods.

XX.—*On Acetoxybenzamic Acid, an Isomer of Hippuric Acid.*

By G. C. Foster.

If we regard hippuric acid as benzoyl-glycocol, or glycocol in which an atom of hydrogen is replaced by benzoyl, it seems natural to expect that an acid isomeric with, and analogous to, hippuric acid, might be obtained by replacing an atom of hydrogen in oxybenzamic acid (syn. benzamic acid, amidobenzoic acid) by acetyl. From the results recorded in this paper, it appears that such is the case.

When oxybenzamic acid is heated in a sealed tube with about half its weight (rather more than one equivalent) of monohydrated acetic acid, the whole mass becomes quite fluid at about 130° or 140°C. but solidifies almost entirely at about 160°, all that remains liquid being the portion of acetic acid used in excess. The reaction which takes place is the following:—

$$\underset{\text{Oxybenzamic acid.}}{C_7H_7NO_2} + \underset{\text{Acetic acid.}}{C_2H_4O_2} = \underset{\text{Acetoxybenzamic acid.}}{C_9H_9NO_3} + H_2O.^*$$

Using at a time from 15 to 20 grammes of oxybenzamic acid, I found that the reaction was quite complete after an hour's heating to 160°, especially if advantage had been taken of the period of complete liquefaction to mix the materials thoroughly.

The same product is also formed by the reaction of chloride of acetyl on oxybenzamate of zinc† at 100°:

$$\underset{\text{Oxybenzamate of zinc.}}{C_7H_6ZnNO_2} + \underset{\text{Chloride of acetyl.}}{C_2H_3OCl} = \underset{\text{Acetoxybenzamic acid.}}{C_9H_9NO_3} + ZnCl.$$

On mixing chloride of acetyl with oxybenzamate of zinc, sufficient heat is given off to volatilize a considerable part of the chloride of acetyl, if care be not taken to condense it, and the whole quickly solidifies to a hard mass (probably a combination of the two substances, analogous to the combination of hydrochloric acid with oxybenzamic acid), which, in a sealed tube at 100°, melts, and then again gradually solidifies; complete solidification indicates the end of the reaction.

Oxybenzamate of zinc heated with two equivalents of acetic acid, or a mixture of equivalent quantities of hydrochlorate of oxybenzamic acid and acetate of calcium with a little acetic acid, yields the same product; but neither of these processes is advantageous, on account of the high temperature required, and the difficulty of thoroughly mixing the materials.

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* $C = 12$, $O = 16$.

† Oxybenzamate of zinc is easily obtained by mixing solutions of chloride of zinc and oxybenzamate of calcium. It separates as a granular precipitate which is very easily washed on a filter. It is nearly insoluble in water, but soluble in acetic acid.

·3624 grm., dried at 100°, was boiled with carbonate of sodium till completely decomposed: the resulting carbonate of zinc yielded on ignition ·0921 grm. oxide of zinc.

	Calculated.	Found.
Zinc per cent.	21·16	20·42

I have found the formation of this salt to be a convenient method of separating oxybenzamic acid from impure solutions.

The substance yielded by these reactions is easily purified. It is sufficient to dissolve it in an alkali, to precipitate the solution by hydrochloric acid, and to crystallize the precipitate two or three times from boiling water or alcohol. Any colouring matter which still adheres to the product thus obtained may be completely removed by animal charcoal.

I have named the new substance *acetoxybenzamic acid.*

Dried over sulphuric acid, it does not lose weight at 100°.

·3788 grm., prepared from acetic and oxybenzamic acids, gave ·8382 grm. carbonic acid, and ·1766 grm. water.

·2913 grm., prepared from chloride of acetyl and oxybenzamate of zinc, gave ·6396 grm. carbonic acid, and ·139 grm. water.

·4363 grm. of another similar preparation gave ·9677 grm. carbonic acid, and ·1987 grm. water.

·4302 grm. of the same product, heated with soda-lime, gave a platinum-salt containing ·2375 grm. platinum.*

·4442 grm. of the same product gave 29·2 cc. nitrogen at 0° and 760 mm. pressure.

	Calculated.		Found.					
								Mean.
C_9	108	60·33	60·36	59·88	60·49	—	—	60·24
H_9	9	5·03	5·18	5·23	5·06	—	—	5·16
N	14	7·82	—	—	—	7·80	8·25	8·02
O_3	48	26·82	—	—	—	—	—	26·64
$C_9H_9NO_3$	179	100·00						100·00

Acetoxybenzamic acid is obtained as a white powder, which, under the microscope, is seen to be formed of needle-shaped crystals. It is almost insoluble in cold water and in ether, and is only moderately soluble in boiling water or in cold alcohol; in boiling alcohol it dissolves easily. It has a slightly bitter taste, a good deal resembling that of nitre. Like its isomer hippuric acid, it dissolves readily in a solution of common phosphate of sodium, giving an acid reaction to the liquid, but is reprecipitated by acetic or a mineral acid. It is soluble in strong sulphuric acid without colouration in the cold, and also in glacial acetic acid; these solutions are precipitated by dilution with water. A mixture of

* In the decomposition of acetoxybenzamic acid by soda-lime very little ammonia is formed; nearly the whole of the nitrogen is given off as aniline.

acetoxybenzamic acid with sufficient strong hydrochloric or nitric acid to make it flow easily becomes nearly solid on standing for a few minutes, but it was found that a mixture of hydrochloric acid and acetoxybenzamic acid loses all its hydrochloric acid when dried under a bell-jar over lime and sulphuric acid.

At about 200° acetoxybenzamic acid sublimes somewhat rapidly; it melts between 220° and 230°, and enters into ebullition at about 260°, apparently undergoing decomposition at the same time. It may be boiled for a long time with water, and even with dilute acids, without undergoing perceptible change; but when heated in a sealed tube with hydrochloric or dilute sulphuric acid to about 140° it is decomposed into oxybenzamic and acetic acids, just as hippuric acid is decomposed under similar circumstances into glycocol and benzoic acid. A quantity of hydrochlorate of oxybenzamic acid thus obtained, gave the following results on analysis:—

·3767 grm., burned with chromate of lead, gave ·677 grm. carbonic acid, and ·1719 grm. water.

·4399 grm. gave ·3624 grm. chloride of silver.

	Calculated.	Found.
Carbon	48·42	49·01
Hydrogen . . .	4·61	5·07
Chlorine	20·46	20·39

Another quantity of acetoxybenzamic acid was decomposed by dilute sulphuric acid of 10 per cent. When the decomposition was complete, the contents of the tube were transferred to a retort and distilled. The distillate was saturated with carbonate of barium, filtered, and evaporated. The barium-salt so obtained proved to be acetate of barium.

·8039 grm., dried at 120°, gave ·7345 grm. sulphate of barium.

	Calculated. $C_2H_3BaO_2$	Found.
Barium per cent. . . .	53·73	53·72

The residue in the retort deposited, on cooling, crystals of sulphate of oxybenzamic acid.

Acetoxybenzamic acid is similarly decomposed by an alcoholic solution of hydrochloric acid, but oxybenzamate and acetate of ethyl are formed at the same time as the corresponding acids. The decomposition takes place slowly in the cold, but quickly at 100°. On distilling the product of the reaction in a water-bath, a light ethereal liquid, possessing the smell and general properties of acetate of ethyl, passed over with the excess of alcohol, and was separated from it by the addition of water. The residue in the retort crystallized on cooling in radiating needles. The crystals, which were very soluble in water and alcohol, but slightly soluble in ether, were recrystallized from water, washed with ether, and dried over sulphuric acid.

·4748 grm. gave ·3501 grm. chloride of silver.
·392 grm. gave ·2924 grm. chloride of silver.
·5091 grm., burned with chromate of lead, gave ·9642 grm. carbonic acid, and ·2638 grm. water.

These results correspond to a mixture of the hydrochlorates of oxybenzamic acid and oxybenzamate of ethyl.

	Hydrochlorate of oxybenzamic acid.	Found.		Hydrochlorate of oxybenzamate of ethyl.
Carbon . . .	48·42	51·65		53·60
Hydrogen . .	4·61	5·76		5·96
Chlorine . . .	20·64	18·24	18·45	17·62

What was left of the crystals, after making the above analyses, was dissolved in water, a slight excess of milk of lime added, and the whole shaken up with ether. The ether left, on evaporation, an oily liquid, apparently oxybenzamate of ethyl, which was nearly insoluble in water, but soluble in hydrochloric acid, giving a chloride insoluble in ether and combining readily with bichloride of platinum. The quantity of the platinum salt obtained was not sufficient for a determination of the percentage of platinum. The aqueous liquid, from which the ether had been poured off, was filtered, and the excess of lime separated by carbonic acid. After being somewhat concentrated by evaporation, it gave with chloride of zinc a precipitate resembling oxybenzamate of zinc.

Attempts were made to obtain acetoxybenzoic acid, $C_9H_8O_4$, isomeric with benzoglycollic acid, by the action of nitric oxide on a mixture of nitric acid and acetoxybenzamic acid, and also by the action of nitrous acid on a boiling aqueous solution of acetoxybenzamic acid, but in both cases the only product was a nitro-substitution compound.

Acetoxybenzamate of potassium was prepared by digesting a solution of the acid in strong alcohol with dry carbonate of potassium. It is exceedingly soluble in water, and dissolves easily in alcohol, but is precipitated from this solution by ether. From a solution in alcohol containing more than about 10 per cent. of water,it is precipitated by ether in the form of a strong aqueous solution which solidifies only after standing for a considerable time.

Acetoxybenzamate of sodium, $C_9H_8NaNO_3 + xH_2O$.—This salt was prepared in the same way as the potassium salt. It is very soluble in water and easily soluble in alcohol, but can be obtained crystallized somewhat more easily than the potassium salt. It is insoluble in ether, and is not deliquescent.

·468 grm., dried between 120° and 130°, gave ·1636 grm. sulphate of sodium.

	Calculated. $C_9H_8NaNO_3$	Found.
Sodium per cent. . .	11·44	11·32

Acetoxybenzamate of barium, $C_9H_8BaNO_3 + 1\frac{1}{2}H_2O$.—Obtained by saturating a hot aqueous solution of the acid with carbonate of barium. It is very soluble in water and crystallizes by the spontaneous evaporation of its solution in minute radiating needles grouped together in tufts. It dissolves readily in spirit of wine, but is precipitated from a strong aqueous solution by absolute alcohol. It loses only a part of its water of crystallization at 100°; for analysis it was dried between 130° and 145°.

1·8854 grm., dried over sulphuric acid, lost ·1812 grm. water between 130° and 145°.

·8776 grm. lost ·0887 grm. water at the same temperature.

·6464 grm. of the dry salt gave ·3027 grm. sulphate of barium.

·3783 grm. gave ·1774 grm. sulphate of barium.

·3918 grm. gave ·1824 grm. sulphate of barium.

·9185 grm., burned with chromate of lead, gave 1·4625 grm. carbonic acid, and ·288 grm. water.

		Calculated.	Found.			
C_9	108	43·81	—	—	—	43·43
H_8	8	3·25	—	—	—	3·48
Ba	68·5	27·79	27·54	27·32	27·42	—
N	14	5·68	—	—	—	—
O_3	48	19·47	—	—	—	—
$C_9H_8BaNO_3$	246·5	100·00				

Substances.	Direction.	Authority.	Hemi-hedral?
Camphoric acid	+ or −	Bouchardat, Chantard	Hem.
Camphoethylic acid	+	Malaguti	Hem.
Camphomethylic acid	+	Loir	Hem.
Naphtha	−	Biot	
Cane-sugar	+	„ Clerget	Hem.
Milk-sugar	+	„ Poggiale	Hem.
Grape-sugar	−	„	
Starch-sugar	+	„ Béchamp	
Diabetes-sugar		„ Clerget, Listing	
Glucosate of sea-salt	+	Pasteur	Hem.
Tartaric acid	+ or −	Biot, Pasteur, Arndtzen	Hem.
Malic acid	+	Pasteur	Hem.
Tartramide	+ or −	„	Hem.
Asparagine	−	„	Hem.
Tartramic acid	+ or −	„	Hem.
Aspartic acid	+	„	
Sulphamylic acid		„	Not
Amylic alcohol		„	
Formobenzoic acid			
Quinic acid			Hem.
Quinine	−	Bouchardat, Pasteur	
Quinidine	+	„ „	
Quinicine	+	Pasteur	
Cinchonine	+	Bouchardat	
Cinchonidine	−	Pasteur	
Cinchonicine	+	„	
Quinoidine	+	Wilhelmy	
Morphine	−	Bouchardat, Pasteur	Hem.
Brucine	−	„	
Strychnine	−	„ Descloizeaux	
Narcotine	+	„	
Nicotine	−	Wilhelmy	
Santonine	−	„	
Hœmatoxylin	+	„	
Jalapin	−	„	
Phloridzin	−	„	
Salicin	−	Bouchardat, Biot and Pasteur	
Populin	−	Biot and Pasteur	
Codeine	−	Bouchardat and Boudet	
Narceine	−	„ „	
Picrotoxine	−	„ „	
Albumin	+	A. Becquerel	

I have not attempted to express in this table the amount of rotatory force possessed by the different substances, not from any lack of numerical data, but for the following reasons :—

1st. It has been frequently determined differently by different observers. This arises to some extent from actual optical differences in the samples employed: thus oil of turpentine is known to possess different powers of rotation, even when the direction remains the same, according to the kind of pine from which it came, and the processes adopted in preparing and purifying it. Again, the amount of solvent employed is a fruitful cause of diversity.

2nd. Unfortunately, in determining the rotatory force, no uniform standard has been adopted. Thus, Biot reduces his observations to a unit of thickness—namely, one millimeter, and he calculates from the arc of rotation of the rays that have passed through red glass. He employs the following formula for determining the specific rotatory power (ρ), in which a stands for the arc of rotation, d the density, and l the thickness or length in millimeters.

$$\rho = \frac{a}{d\,l}$$

And if the substance be dissolved in some optically neutral solvent, the proportion of the said substance in one part of the solution (p) has to be taken into account, and the formula stands—

$$\rho = \frac{a}{d\,l\,p}$$

Wilhelmy,[*] on the contrary, laying stress on the molecular nature of the force, considers it preferable to take the different substances in quantities proportional to their atomic weights in equal weights of the solvent; and where he cannot do this, he makes a reduction on the hypothesis that the relative quantity of the solvent has no influence. He makes his calculations also for white light, and assumes the molecular rotating power of cane sugar as 100.

A table given in one of Wilhelmy's papers[†] is so good an illustration of the elaborate investigations that have been made into this subject, that I have reproduced it here.

Substance.	Quantity dissolved	Solvent.	Degree of rotation.		Atomic weight. O = 100.	Molecular rotating power. (White light.)
			White Light.	Red Light.		
	milligr.					
Cane-sugar	4309	Water	+ 32°5	+ 25°	2154·5	+ 100
Nicotine	1301	Alcohol	− 16			
—— with hydrochloric acid	"	"	+ 1(?)			
Santonin	500	"	− 9	+ 6·7	3005	− 332·3
Hematoxylin	1849	"	..	+ 13·5		
Jalapin	2000	"	..	− 7		

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[*] Pogg. Ann., lxxxi, 413, 499.

[†] Ibid, lxxxi, 527.

Substance.	Quantity dissolved	Solvent.	Degree of rotation.		Atomic weight. O = 100.	Molecular rotating power. (White light.)
			White Light.	Red Light.		
	milligr.					
Camphor	6000	Alcohol	+31°	+22°	963·8	+30·7
Phloridzin	2377	„	−11	−8·7	2082·5	−59·2
Quinine	1782	„	−24	−20	2055·5	−174
——	891	„	−12·5	−9·65		
—— with nitric acid ..	„	„	−17	..	..	−241·4
—— with phosphoric acid	„	„	−15	..	..	−213
Sulphate of quinine ..	1000	Water & sulp. acid	−24·5	−16·7		
Valerate of quinine ..	„	Alcohol	−16	−13		
Hydrochlorate of quinine ..	500	„	−10			
Cinchonine	454	„	+12	..	1942	+315·8
—— with oxalic acid ..	494	„	+12·5	..	..	+302
—— with phosphoric acid	952	„	+23·5	..	..	+295
—— with nitric acid ..	930	„	+20	..	..	+257
—— „ „ ..	465	„	+10			
Quinoidine	374	„	+9·5	+8		
—— with nitric acid ..	„	„	+9·75			
—— with phosphoric acid ..	„	„	+10			
—— with hydrochloric acid	„	„	+10			
—— with sulphuric acid ..	„	„	+11·5			
Brucine	984	„	−8	..	3448	−172·5
—— with phosphoric acid	„	„	0			
Narcotine with sulphuric acid	936	Water	+5·5	..	4684	+169
Acetate of morphine ..	490	„	−4			
Hydrochlorate of codeine ..	578	„	−5			
Ethereal oil of cubebs ..	7460	Alcohol	−33·5			
——— „ valerian ..	7480	Ether	−15·4			
Balsam of copaiva	7560	Ether with alch.	−11·5			

Influence of state of Aggregation.—The only substance which has been examined in the three different states of aggregation—the solid, liquid, and gaseous, is oil of turpentine, and it has been found to exhibit the power in each of these states. It rotates the plane of polarization to the same extent when frozen as when in its ordinary liquid condition; but Biot, who made the experiment on the vapour of turpentine, was unable to determine whether the power was then altered in amount. It was necessary, as will be readily understood, to look through a large amount of the vapour in order to observe any effect on polarized light; in fact, an iron tube 15 metres, that is 50 feet, long was employed for the experiment, and unfortunately before the quantitative determination was completed, a burst of flame occurred, and gave rise to a conflagration which the philosopher could not extinguish without the assistance of the public.

Yet, while oil of turpentine is so retentive of this power, its very existence in some other substances appears to depend on the manner in which they are crystallized. Thus silica does not show any effect on polarized light as it exists in the opal, or indeed in any other form than that of quartz-crystal.

Influence of temperature.—Just as the refrangibility of a substance changes with alterations of the temperature, and that not *pari passu* with the change of density, so also the amount of rotatory power varies under like circumstances. There are however great differences between one substance and another in this respect.

Quartz shows an increased power of rotating the plane of polarization when it is heated, and that to the extent of 108° or 109·5° for an elevation of 70° C. of temperature. This crystal is known to expand by heat differently in the direction transverse to what it does in that parallel to its axis.

Tartaric acid is similarly affected, and that to such an extent that Biot found himself able, by reducing the temperature, actually to reverse the direction of the rotation in solid amorphous tartaric acid, the right-handed deviation diminishing, becoming *nil,* and the left-handed commencing before the thermometer sank to 3° C.

Grape-sugar in solution is much effected by changes of temperature; and in saccharimetry by means of polarized light, account must be taken of this circumstance. Clerget,* who has studied this subject, finds that the power of rotation decreases—not increases—as the temperature rises, and that according to the quantity of sugar, quite irrespective of the proportion of water; indeed, it is the same whether 100 parts of water dissolve 1 or 130 parts of sugar. He found the decrease between 10° C. and 35° C. to be in the proportion of very nearly 100 to 91. Wilhelmy has determined it for a much longer range of temperature, and deduced the formula

$$D' = D\ [1 - 0{\cdot}012\ (t' - t)]$$

in which D and D′ represents two amounts of rotation corresponding with the temperatures t and t'.

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* Ann. Ch. Phys., [3] xxvi, 175.

Salts of quinine, and many other substances, are also known to vary in their power of rotating a ray of polarized light according to the temperature.

Yet, on the other hand, it is stated that the essential oil of turpentine has exactly the same power at 55° C. as at 10° C., and even when frozen.

Influence of Magnetism or Electricity.—I cannot help alluding to the beautiful discovery of Faraday, that a polarized ray passing through optically inactive bodies may be caused to rotate by the magnetic or electric force, and that the rotation in active bodies, such as oil of turpentine, may be altered, or even reversed, at will. This part of the subject, however, I must not pursue further, as it belongs purely to the domain of physics.

Influence of Solution.—Substances which exhibit circular polarization are affected by solution in three different manners.

1st. There are substances, as chlorate of soda, bromate of soda, and the double acetate of uranic oxide and soda, the crystals of which exhibit evidences of circular polarization, but are perfectly inactive when dissolved in water.* These bodies, like quartz, appear to owe this property to the manner in which their molecules are arranged in the crystals.

2nd. There are other substances, all of them organic, which exhibit the same polarizing power, whether they are in the solid state or dissolved in some optically neutral solvent, such as water or alcohol. This cannot generally be determined, as in most crystals of such bodies the phenomena of circular polarization are masked by the double refraction; but "barley-sugar" has been found to have the same or nearly the same power of rotation as the sugar when dissolved in water; and it has been recently shown that, whatever the amount of water in which it is dissolved, the rotatory power of sugar is rigorously constant.† Oil of turpentine belongs to this class. In such cases, the substances seem to owe their power of rotating the plane of polarization to the very structure of their molecules.

3rd. There are other substances in which the result partakes to a certain extent of both these characters, where, indeed, it would seem that the individual action of the molecules is accompanied in the solid state by another action arising from their regular arrangement. Thus sulphate of strychnine* evaporated at a temperature of between 10° C. and 20° C. gives a salt which contains 13 atoms of water. It crystallizes in the system of the rectangular prism with a square base, and is of such a form as to allow the recognition of the circularly polarizing power. It rotates the ray, in fact, to about half the extent that left-handed quartz does; but the solution of sulphate of strychnine in water, though it also rotates the plane, does so only to $\frac{1}{24}$th or $\frac{1}{25}$th part of the extent to which these crystals do.

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* Marbach, Ann. Ch. Phys, [3] xliii, 252, xliv, 41. Biot confirms and draw philosophical deductions from these experiments.

† Arndtzen, Ann. Ch. Phys., [31] iv, 403.

Tartaric acid when obtained in a transparent, solid, amorphous state by mixing it with boracic acid, was found to exhibit circular polarization; but different proportions of water cause very remarkable, and as yet unexplained, differences in the optical character of a solution of tartaric acid. The plane of polarization of the green rays is in fact caused to deviate more than that of any other colour, and Arndtzen, who has worked out the whole of this matter with much care and ability, found when operating with ordinary (that is right-handed) tartaric acid dissolved in alcohol instead of water, that he could obtain a left-handed rotation for the blue rays. The same observer found, in reference to camphor dissolved in alcohol, that the rotatory power augments with the refrangibility of the rays more rapidly than in the case of most active bodies, and that the rotatory power decreases regularly with the concentration of the solution.†

Influence of Chemical Combination or Substitution.—In most cases this property appears to be so intimately connected with the structure of the molecule itself, that it is unaffected, or little affected, by chemical changes of an important character.

Thus an optically active acid, such as tartaric acid, will carry its rotatory power into its salts; and similarly an optically active base, such as quinine, will exhibit the phenomena of circular polarization when combined with inactive acids. From observations on neutral and bitartrate of potash and ammonia, which are isomorphous, Pasteur‡ has drawn the conclusion that when quantities of isomorphous substances corresponding to the equivalents are dissolved in equal quantities of water, these solutions rotate the plane of polarization to an equal degree. But it must not be supposed that as a general rule the optically inactive base or acid exerts no modifying influence on the phenomena exhibited by the active element with which it is combined. A glance at the above quoted table of Wilhelmy will show that it is otherwise. Bouchardat* has given numbers which indicate that the combination of camphoric acid with soda or with ammonia reduces its rotatory power; some malates have a positive, others a negative rotation; and, as a further example, asparagine if dissolved in pure water or in alkalis turns the plane of polarization to the left, but if in mineral acids, it turns it to the right.†

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* Descloizeaux, Ann. Ch. Phys., [3] li, 361.

† Ann. Ch. Phys., [3] liv, 403. Biot had experimented on these matters previously; see Ann. Ch. Phys., [3] xxxvi, 257, 405.

‡ Inst., 1850, 339.

Oxidation even does not necessarily destroy this power, for camphor retains it when it has been oxidized into the camphoric acid just alluded to; nor does the substitution of a compound radicle for hydrogen, as is shown by the optical properties of camphovinic‡ and camphomethylic acids.§ The conversion of an acid into an amide, and that again into the corresponding amidogen-acid, is not even fatal to the retention of this optical power, as is evidenced by the activity not only of tartaric acid, but also of tartramide and tartramic acid; and, in a parallel manner not only of malic acid, but also of malamide and malamic acid—that is, asparagine and aspartic acid.‖

It must, however, be supposed in reference to every circularly polarizing substance, that there is some amount of chemical change which the molecule cannot suffer without losing this property. In the case of the two acids just mentioned, tartaric and malic, we find this point passed, when by the action of heat they are converted into other acids, with evolution of part of their constituent elements: for pyrotartaric, fumaric, and maleic acids have no effect on the polarized beam.¶ And here must be mentioned one of Pasteur's remarkable observations. From fumarate of ammonia, which is inactive, aspartic acid may be produced; but this, unlike ordinary aspartic acid, is itself inactive; and again from this may be reproduced malic acid, which also in its turn, unlike that derived directly from the plant, has no influence on the polarized beam.*

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* Comp. rend., xxviii, 319.
† Pasteur, Ann. Ch. Phys. [3] xxxi, 67.
‡ Malaguti.
§ Loir, Ann. Ch. Phys., [3] xxxviii, 483.
‖ Pasteur, Ann. Ch. Phys. [3] xxxviii, 437.
¶ Ibid, xxxi, 67.

As yet we have no evidence that an optically active substance has ever been artificially prepared from one that is optically inactive, though such is constantly occurring in nature. The tartaric acid which Liebig has very recently prepared has been found to rotate the plane of polarization like natural tartaric acid,† but then it must be borne in mind that it was prepared from milk-sugar, which is itself endowed with this property. It will be interesting to determine whether the tartaric acid which Perkin and Duppa have just succeeded in preparing from succinic acid exhibits this power, for succinic acid as yet is not classed among those bodies which display it. Yet from its analogy to tartaric and malic acids, it would appear highly probable that succinic acid should rotate the polarized beam. A specimen said to have been prepared from stearic acid was found by me to be perfectly inactive; but it is quite possible that the succinic acid prepared from malic acid, or that which Dessaignes‡ announces he has prepared from tartaric acid, may prove capable of rotating a ray of light.

The mutual relationship of the substances here referred to will be readily understood by a reference to the following table :

	$C = 6;\ O = 8$	$C = 12;\ O = 16$
Tartaric acid . .	$2HO.C_8H_4O_{10}$	$C_4H_6O_6$
Malic acid . .	$2HO.C_8H_4O_8$	$C_4H_6O_5$
Succinic acid . .	$2HO.C_8H_4O_6$	$C_4H_6O_4$
Tartramide . .	$C_8H_8N_2O_8$	$C_4H_8N_2O_4$
Asparagine . .	$C_8H_8N_2O_6$	$C_4H_8N_2O_3$
Tartramic acid .	$HO.C_8H_6NO_9$	$C_4H_7NO_5$
Aspartic acid . .	$HO.C_8H_6NO_7$	$C_4H_7NO_4$
Pyrotartaric acid .	$HO.C_6H_3O_5$	$C_3H_4O_3$
Fumaric acid . .	$2HO.C_8H_2O_6$	$C_4H_4O_4$
Maleic acid . .	$2HO.C_8H_2O_6$	$C_4H_4O_4$

Relation between Crystalline Form and the power of Circular Polarization.—As far back as 1820 Herschel found that the crystals of right-handed and of left-handed quartz differ in form, and from the inclination of certain facets he was able to foretel what would be the direction of the rotation in any particular specimen;* but it was reserved for Pasteur to show that this relation between the crystalline form and the rotatory power is one that generally obtains.

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* Ann. Ch. Phys., [3] xxxiv, 30.

† Bohn, Ann. Ch. Pharm., Jan, 1860.

‡ Compt. rend., April 16, 1860.

It is well known that the law of symmetry does not hold good in all crystals. These exceptional forms have been termed hemihedral. It will sometimes happen also that a substance will crystallize in two forms which are both unsymmetrical, but unsymmetrical in opposite directions—that is to say, the one form will appear identical with the other only when it is seen reflected in a mirror. They differ, in fact, in the same way as one side of our face differs from the other, or as our two hands differ. These are variously called not superposable, incongruous, or opposite hemihedra.

From an observation of the opposite hemihedral character of crystals of the double racemate of soda and ammonia, Pasteur commenced that series of observations which led him to the discovery that racemic acid is composed of two tartaric acids, with opposite but equal powers of polarization, conjoined together as one substance; to the isolation of left-handed tartaric acid; to the artificial preparation of racemic acid; and of a neutral and unresolvable tartaric acid†—discoveries which, however interesting, I refrain from dwelling on, as the papers in which they are explained have been printed in our Quarterly Journal, and are well known to chemists in this country.

The same philosopher has shown by a great number of instances that when a substance crystallizes in opposite hemihedra, it indicates the existence of two opposite powers of rotation, and that active and inactive bodies will not crystallize together, however isomeric.‡ Yet it cannot be laid down as a universal law that this property of matter in a crystalline state is always accompanied with the power of circular polarization, for formate of strontia gives opposite hemihedra, but neither kind of crystal when separated from the other and dissolved, has any influence on polarized light.§ Sulphate of magnesia is an analogous instance. Nor, on the other hand, can it be affirmed that this optical property is necessarily connected with the power of forming such crystals; for two sulphamylic acids have been discovered which are isomeric, and absolutely identical in the crystalline form of their salts, without showing any disposition to form hemihedra, and yet the one is active and the other inactive.*

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* See his remarks on this subject in his article on Light in the Encyc. Metrop., par. 1042, in which he almost prophecies more recent discoveries.

† Ann. Ch. Phys., [3] xxiv, 442; xxviii, 56, and Compt. rend., xxxvii, 162.

‡ Ann. Ch. Phys. [3] xxxviii, 437.

§ Ibid, xxxi, 67.

The inactive aspartic acid derived from fumarate of ammonia does not crystallize in hemihedra, as the ordinary aspartic acid does; and similarly there are some differences in the crystalline forms of the salts of the natural or active, and of the artificial or inactive malic acid.

Marbach† has observed that though chlorate of soda crystallizes in opposite hemihedra, and in that condition exercises an influence on the polarized beam, yet a solution of either right-handed or left-handed crystals alone is perfectly inactive, and the salt crystallizes out from such a solution in *both* forms instead of that only from which it was made.

CIRCULAR POLARIZATION AS APPLIED TO CHEMICAL INQUIRIES.

The phenomena of circular polarization have been applied to many practical purposes in chemical research. These may be conveniently grouped under three heads—the quantitative estimation of certain organic products; the determination of what is going forward in a solution; and the examination of isomeric substances.

1st. *Quantitative estimation of certain organic products.*

Cane Sugar.—As cane sugar dissolved in water rotates the ray of polarized light to an extent directly proportional to the amount of sugar in a given depth of liquid, and irrespective of the amount of water, or of the simultaneous presence of optically inactive substances, this property is frequently made use of to effect a quantitative determination. Clerget‡ has worked out this process very fully, and others§ have since somewhat extended or modified his observations. Instruments have been devised for the purpose by Biot, Soleil,* Savart, Powell,† Leeson,‡ Mitscherlich, but the simplest, and perhaps the most effective, is a modification of Biot's apparatus which Mr. Heisch employs, and has kindly lent me on this occasion. It consists essentially of three parts—a polarizer, an analyser, and a tube for holding the solution. The polarizer is a Nicoll's prism and plano-convex lens to render the rays parallel; the analyser consists of a small aperture in a brass plate, a lens, and an achromatic prism of doubly refracting spar, and it is attached to the vernier of a graduated circle. The tube through which the polarized beam passes between the polarizer and the analyser is a narrow tube of black glass ground in the inside with coarse emery, and fitted at each end with covers of perfectly parallel glass. Several such tubes of various known lengths, so as to hold different quantities of liquid are provided, and the position of the polarizer and analyser can be easily adapted to each. If when the index of the scale is at 0°, and the extraordinary image is at its greatest obscuration, a solution of sugar be placed in the tube, it is easy to determine how much the analyser must be now turned round in order to bring the extraordinary image again to its greatest obscuration, or rather to the "sensitive tint." It is impossible here to enter into the minutiæ of the apparatus, or of the treatment of the solution; suffice it to say that Heisch prefers operating by lamp light, and has found that it requires 6·09 per cent. of cane-sugar to produce a rotation of 1° in a depth of 1 inch: hence the percentage in the solution examined may be reckoned according to the simple formula

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* Compt. rend., xlii, 1259.

† Ann. Ch. Phys., [3] xliv, 41.

‡ Ibid. xxvi, 175.

§ Especially Wilhelmy and Arndtzen, in papers previously referred to; Pohl, Wien. Acad. Bericht, xxi, 492; and Michäelis, Journ. Pharm. Chem., lxxv, 464.

$$p = 6{\cdot}09 \frac{a}{l}$$

a representing the arc of rotation, and l the length in inches.

An ingenious method of confirming the amount of cane-sugar in a solution, or of determining it in the presence of other optically active bodies, is founded on the property possessed by this sugar of being converted by acids into a sugar which exhibits the opposite or left-handed rotation. The following formula serves for this inverted sugar, according to Heisch, at 15° C.

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* The English reader will find a description of this instrument by Dr. Bence Jones in the Pharm. Journ. and Trans., xi, 455.

† Phil. Mag., April, 1843.

‡ Mem. Chem. Soc., ii, 26.

$$p \quad = \quad 16{\cdot}026 \frac{a}{l}$$

As glucose rotates the plane of polarization to the right, and is not capable of inversion by acids, this process will even serve to determine the respective amounts of cane-sugar and glucose if mixed together in solution. Or the same may be effected by determining the rotation of the mixed solution, boiling it with potash, which destroys the glucose, and then again determining the rotation which is now due solely to cane-sugar.

Other sugars.—Bence Jones* has published analyses of the different wines of commerce, in which he determined the grape-sugar by means of Soleil's saccharimeter.

Poggiale† has employed a similar method for the estimation of the amount of sugar in milk.

Listing‡ has published optical determinations of the sugar in diabetic urine. The formula of Heisch for this sugar is

$$p \quad = \quad 8{\cdot}346 \frac{a}{l}$$

If albumin be present, it must be removed, as it possesses itself an influence on polarized light.

Albumin.—This substance may likewise be estimated by means of its rotating power, and A. Becquerel§ has in fact measured in this way the proportion of albumin contained in the serum of blood.

2nd. *Determination of what is going forward in a solution.* The variations in the plane of polarization will often indicate changes in a solution which could not be watched by any other method, or even the existence of which might never otherwise have been recognized.

Thus Wilhelmy‖ investigated the action of sulphuric, phosphoric, nitric, and hydrochloric acids on cane-sugar, and examined mathematically the progress of the change with reference to time. He satisfied himself that the final result of the conversion of the sugar is independent of the quantity of acid originally added.

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* Proc. Roy. Inst. Vol. i.

† Compt. rend., xxviii, 505, 584.

‡ Ann. Ch. Pharm., xcvi, 93, 101.

§ Compt. rend., xxix, 625.

‖ Pogg. Ann. lxxxi, 413, 499.

Biot investigated a very curious state of combination between tartaric acid and boracic acid when they are both dissolved together in water, and he endeavoured to determine the nature of the transformation which tartaric acid undergoes when acted on by heat. He has applied circular polarization also more widely to the study of the question of the condition of a substance in solution. The papers* which contain these inquiries are very lengthy, and include much philosophical reflection on the subject in general.

Thus also, from some observations of Bouchardat on the effect of polarized light on camphoric acid, the same saturated with soda, and then supersaturated with hydrochloric acid, I was able to derive from a novel source an additional illustration of the reciprocal decomposition of binary compounds in solution.†

Béchamp‡ too, from observations with the polariscope, arrived at the conclusion that crystallized starch sugar is a combination which cannot exist indefinitely except in the solid state, and that when dissolved in water it loses its combined water, slowly in the cold, but rapidly under the influence of heat, resembling in this respect hydrated oxide of copper or hydrated oxide of iron in the presence of water. In fact he supposes that the $C_{12}H_{12}O_{12}.2HO$ when dissolved passes, during the lapse of a certain number of hours, wholly into $C_{12}H_{12}O_{12}$.

3rd. *Examination of isomeric substances.*

Reference has already been made to the researches of Pasteur by which he unravelled the relations between racemic and tartaric acids, and enriched our knowledge of many organic compounds by exhibiting isomeric bodies identical with them save in their action on polarized light, and perhaps their crystalline form. Their solubility appears also in some instances to be slightly affected. His discoveries however have not been confined to those already alluded to. Finding that there exist two sulphamylic acids, the one possessed of the rotatory power and the other not possessing it, he was able by their decomposition to produce two amylic alcohols differing slightly in their physical properties.§ His very original examination of the cinchona alkaloids, and the two isomeric groups at the head of which stand quinine and cinchonine,[*] I shall only just refer to, as his paper was reproduced in our Quarterly Journal.[†]

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* Ann. Ch. Phys., xxviii, 215, 351; xxxvi, 257, 405.

† Chem. Soc. Qu. J., ix, 148.

‡ Compt. rend., xlii, 640. Dubrunfaut differs from this explanation, *ibid*, 739; but Béchamp defends his own view, *ibid*, 896.

§ Comp. rend., xlii, 1259.

Different isomeric essential oils of the composition C_5H_4 might be distinguished by this method, but the data seem wanting for the practical application of circular polarization to the analysis of them.

Berthelot[‡] has by the same agency investigated a very remarkable change that takes place in oil of turpentine, or oil of lemons, by the action of acids, alkaline or earthy chlorides, or some other salts. This isomeric modification is indicated by a reduction of the rotatory power whether positive or negative; it never entirely disappears, but there are grounds for believing that the result is a mixture of unaltered oil, and oil which has been rendered inactive. It is not necessary that the salt which produces this singular change should dissolve in the oil, for even the insoluble fluoride of calcium has a strongly marked effect.

XXIV.—ON CHEMICAL ANALYSIS BY SPECTRUM-OBSERVATIONS.

By Professors KIRCHHOFF and BUNSEN.

(From Poggendorff's Annalen, Bd. cx. S. 161.)

It is well known that many substances possess the power of developing peculiar bright lines in the spectrum of a flame into which they are introduced. This property may be made the foundation of a method of qualitative analysis, which greatly enlarges the field of chemical reactions, and leads to the solution of problems hitherto unapproachable.

The bright lines produced in this manner, show themselves most plainly when the temperature of the flame is highest and its illuminating power least. Hence Bunsen's gas-burner, which gives a flame of very high temperature and very slight luminosity, is well adapted for experiments on the bright lines of the flame-spectra produced as above described.

The coloured plate at the end of this paper, shows the spectra given by such a flame when the chemically pure chlorides of potassium, sodium, lithium, strontium, calcium, and barium are volatilised in it. The ordinary solar spectrum is added by way of comparison.

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[*] Comp. rend., xxxvii, 110.

[†] Vol. vi, p. 273.

[‡] Ann. Ch. Phys., [3] xxxviii, 38.

The potassium compound employed was obtained by igniting chlorate of potassium which had been previously recrystallized six or eight times. The chloride of sodium was prepared by neutralizing pure carbonate of sodium with hydrochloric acid and crystallizing the salt several times.

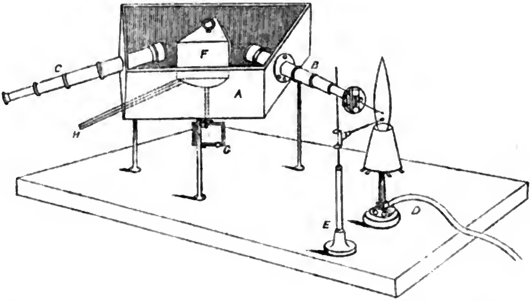
The salt of lithium was purified by precipitation fourteen times with carbonate of ammonium.

The purest specimen of marble which could be obtained, dissolved in hydrochloric acid, was the source of the calcium salt. From this solution the carbonate of calcium was thrown down in two portions by fractional precipitation with carbonate of ammonium, the latter half of the calcium salt being converted into the nitrate. The salt thus obtained was dissolved in absolute alcohol, and after evaporation of the alcohol, converted into the chloride by precipitation with carbonate of ammonium and solution in hydrochloric acid.

To obtain pure chloride of barium, the commercial salt was boiled out repeatedly with nearly absolute alcohol, and the residual salt freed from alcohol was dissolved in water, and thrown down by fractional precipitation in two portions. The second only of these portions was dissolved in hydrochloric acid, and the salt still further purified by repeated crystallizations.

Pure chloride of strontium was prepared by crystallizing the commercial salt several times from alcohol, and by fractional precipitation of the salt with carbonate of ammonium, the second portion being dissolved in nitric acid, and the nitrate freed from the last traces of calcium salt by boiling with alcohol. The product thus purified was lastly thrown down with carbonate of ammonium, and the precipitate dissolved in hydrochloric acid. All these various purifications were conducted as much as possible in platinum vessels.

The apparatus which we have usually employed for our spectrum-observations is represented in the annexed woodcut. A is a box blackened on the inside, having its horizontal section in the form of a trapezium, and resting on three feet; the two inclined sides of the box, which are placed at an angle of about 58° from each other, carry the two small telescopes B and C. The eye-piece of the first telescope is removed, and in its place is inserted a plate, in which a slit made by two brass knife-edges is so arranged that it coincides with the focus of the object-glass. The gas-lamp D stands before the slit in a position such that the mantle of the flame is in a straight line with the axis of the telescope B. Somewhat lower than the point at which the axis of the tube produced meets the mantle, the end of a fine platinum wire bent round to a hook is placed in the flame. The platinum wire is supported in this position by a small holder, E, and on to the hook is melted a globule of the dried chloride which it is required to examine. Between the object-glasses of the telescopes B and C is placed a hollow prism, F, filled with bisulphide of carbon, and having a refracting angle of 60°. The prism rests upon a brass plate moveable about a vertical axis. The axis carries on its lower part the mirror G, and above that the arm H, which serves as a handle for turning the prism and mirror. A small telescope placed some way off is directed towards the mirror, and through this telescope an image of a horizontal scale, fixed at some distance from the mirror, is observed. By turning the prism round, every colour of the spectrum may be made to move past the vertical wire of the telescope C, and any required position in the spectrum thus brought to coincide with this vertical line. Each particular portion of the spectrum thus corresponds to a certain point on the scale. If the luminosity of the spectrum is very small, the wire of the telescope C may be illuminated by means of a lens, which throws a portion of the rays from a lamp through a small opening in the side of the tube of the telescope C.



We have compared the spectra represented on the Plate, which were obtained from the pure chlorides, with those produced when the bromides, iodides, hydrates, sulphates and carbonates of the several metals are brought into the following flames:—

Into the flame of sulphur.
" " bisulphide of carbon.
" " aqueous alcohol.
Into the non-luminous flame of coal-gas.
Into the flame of carbonic oxide.
" " hydrogen.
Into the oxyhydrogen flame.

As the result of these somewhat lengthy experiments, the details of which we here omit, it appears that neither the alteration of the bodies with which the several metals may be combined, nor the variety of the chemical processes occurring in the several flames, nor the wide differences of temperature which these flames exhibit, *produce any effect upon the position of the bright lines in the spectrum which are characteristic of each metal.*

The following considerations show how much the temperature of these various flames differ. An approximation to the temperature of a flame is obtained by help of the equation.

$$t = \frac{\Sigma gw}{\Sigma ps},$$

in which t signifies the required temperature of the flame, g the weight of one constituent of substance burning in oxygen, w the heat of combustion of this constituent, p the weight, and s the specific heat of one of the products of combustion. The heat of combustion of the following bodies may be taken as—

Sulphur	2240° C.
Bisulphide of carbon	3400
Hydrogen	34462
Marsh-gas	13063
Ethylene	11640
Butylene	11529
Carbonic oxide	2403

The specific heats under constant pressure were found by Regnault to be—

Sulphurous acid $= 0{\cdot}1553$
Carbonic acid $= 0{\cdot}2164$
Nitrogen $= 0{\cdot}2440$
Aqueous vapour $= 0{\cdot}4750$

Hence the temperatures of the flames are found to be—

The sulphur flame	1820° C.
The bisulphide of carbon flame	2195
The coal-gas flame*	2350
The carbonic oxide flame†	3042
The hydrogen flame in air‡	3259
The oxyhydrogen flame§	8061

It was found that the same metallic compound, placed in one of these flames, gives a more intense spectrum the higher the temperature of the flame. In the same flame, those compounds of a metal give the brightest spectra which are most volatile.

In order to prove still more conclusively that each of the above-mentioned metals always produces the same bright lines in the spectrum, we have compared the spectra represented in the Plate with those produced when the electric spark passes between electrodes made of these metals.

Small pieces of sodium, potassium, lithium, strontium, and calcium were fastened to fine platinum wires and melted two by two into glass tubes, so that the pieces of metal were separated by about 1 to 2 millims., and the platinum wires were melted through the sides of the glass tubes. Each of these tubes was placed in front of the spectrum-instrument, and by means of a Ruhmkorff's induction apparatus, sparks were allowed to pass between the pieces of metal inside the tube; the spectrum thus produced was then compared with that given by a gas-flame into which the chloride of the metal was brought. The flame was placed behind the glass tube. By alternately bringing the induction apparatus into and out of action, it was easy, without measuring, to convince ourselves that in the brilliant spectrum of the electric spark, the bright lines of the flame-spectrum were present in their normal position. Besides these lines, other bright ones appeared in the electric spark spectrum; some of these were produced by foreign metals present in the electrodes; others arose from nitrogen, which filled the tubes after the oxygen had combined with a portion of the electrodes.*

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* Ann. Ch. Pharm. cxi. 258.

† Bunsen's 'Gasometry.' p. 242.

‡ Ibid.

§ Ibid.

From these facts it appears certain that the appearance of the bright lines represented in the spectra on the Plate may be regarded as absolute proof of the presence of the particular metal. They serve as reactions by means of which these bodies may be recognized with more certainty, greater quickness, and in far smaller quantities than can be done by help of any other known analytical method.

The spectra drawn on the Plate represent those seen when the slit was of such a width that only the most conspicuous of the lines of the solar spectrum were visible, the magnifying power of the telescope C being a fourfold one, and the light of a moderate degree of intensity. These circumstances seem to us to be the most advantageous when it is required to make a chemical analysis by means of spectrum-observations. The appearance of the spectrum may, under other conditions, be essentially different. If the purity of the spectrum be increased, many of those lines which appeared before as single ones are split up into several; thus the sodium line is divided into two separate lines. If, on the other hand, the intensity of the light be increased, new lines appear in several of the spectra and the relative brightness of the old ones becomes altered. In general an indistinct line becomes brighter upon increasing the illumination, more rapidly than a brighter line, but not to such an extent that the indistinct line ever overtakes the brighter one in intensity. A good example of this is seen in the two lithium lines. We have observed only one exception to this rule, namely in the line Ba η, which by light of small intensity is scarcely visible, whilst Ba γ appears plainly, but by light of greater intensity becomes more visible than the latter. We intend on a future occasion to examine this point in detail.

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* On employing on one occasion with strontium-electrodes a tube filled with hydrogen instead of nitrogen, the stream of sparks changed rapidly into a continuous arc of light, whilst a grey pellicle covered the inside of the tube. The tube was opened under rock-oil, when it was found to be empty, the hydrogen having disappeared. This gas appears, at the enormously high temperature of the electric spark, to have decomposed the oxide of strontium which was not completely removed from the metal.

We now proceed to describe the peculiarities of the several spectra, the exact acquaintance with which is of practical importance, and to point out the advantages which this new method of chemical analysis possesses over the older processes.

Sodium.

The spectrum-reaction of sodium is the most delicate of all. The yellow line Na α, the only one which appears in the sodium spectrum, is coincident with Fraunhofer's dark line D, and is remarkable for its exactly defined form, and its extraordinary brightness. If the temperature of the flame be very high, and the quantity of the substance employed very large, traces of a continuous spectrum are seen in the immediate neighbourhood of the line. In this case too, the weaker lines produced by other bodies, when near the sodium line, are discerned with difficulty, and are often not seen till the sodium reaction has almost subsided.

The reaction is most visible in the sodium-salts of oxygen, chlorine, iodine, bromine, sulphuric acid, and carbonic acid; but it is always evident, even in the silicates, borates, phosphates, and other non-volatile salts.

Swan* has already remarked upon the small quantity of sodium necessary to produce the yellow line.

The following experiment shows that the chemist possesses no reaction which will bear the remotest comparison, as regards delicacy, with this spectrum-analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about 60 cubic metres, we burnt a mixture of 3 milligrammes of chlorate of sodium with milk-sugar, whilst the non-luminous flame of the lamp was observed through the slit of the telescope. Within a few minutes, the flame, which gradually became pale yellow, gave a distinct sodium line, lasting for ten minutes, and then entirely disappearing. From the weight of sodium salt burnt, and the capacity of the room, it was easy to calculate that in one part by weight of air there was suspended less than $\frac{1}{20,000,000}$ of a part of soda-smoke. As the reaction can be quite easily observed in one second, and as in this time the quantity of air which is heated to ignition by the flame is found, from the rate of issue and from the composition of the gases of the flame, to be only about 50 cub. cent. or 0·0647 grm. of air, containing less than $\frac{1}{20,000,000}$ of sodium salt, it follows that the eye is able to detect with the greatest ease quantities of sodium salt less than $\frac{1}{3,000,000}$ of a milligramme in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried into the air by the action of the waves. The particles of sea-water thus cast into the atmosphere, evaporate, leaving almost inconceivably small residues, which, floating about, are almost always present in the air, and are rendered evident to our eyesight in the sunbeam. These minute particles perhaps serve to supply the smaller organized bodies with the salts which larger animals and plants obtain from the ground; but there is also another point of view, in which the presence of this chloride of sodium in the air is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact-action, it is possible that the presence of an antiseptic substance like chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere. By means of daily and long-continued spectrum observations, it would be easy to discover whether the alteration of intensity in the line Na *a* produced by the presence of sodium-compounds in the air, has any connection with the appearance and direction of march of an endemic disease.

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* Trans. Roy. Soc. Edinb. vol. xxi. Part III. p. 411.

The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies, after a lengthened exposure to air, show the sodium line when brought into a flame, and that it is only in a few salts that it is possible to get rid of the last traces of the line Na *a*, even after repeated crystallization from water which has only been in contact with platinum. A thin platinum wire, freed by ignition from every trace of sodium salt, shows the reaction most visibly after a few hours' exposure to the air. In the same way, the dust which settles from the air in a room, shows the bright line Na *a*: to render this evident it is only necessary to knock a dusty book, for instance, at a distance of some feet from the flame, when a wonderfully bright flash of the yellow band is seen.

Lithium.

The luminous ignited vapour of the lithium compounds gives two sharply defined lines, the one a very weak yellow line, Li *β*, and the other a bright red line, Li *a*. This reaction likewise exceeds in certainty and delicacy all ordinary methods of analytical research. It is, however, not quite so sensitive as the sodium reaction, only, perhaps, because the eye is more adapted to distinguish yellow than red rays. When 9 milligrammes of carbonate of lithium mixed with excess of milk-sugar were burnt, the reaction was visible in a room of 60 cubic metres capacity.

Hence, by the method already explained, we find that the eye is capable of distinguishing with absolute certainty a quantity of carbonate of lithium less than $\frac{9}{10,000,000}$ of a milligramme in weight: 0·05 grm. of carbonate of lithium salt, burnt in the same room, was sufficient to enable the ignited air to show the red line Li *a* for an hour after the combustion had taken place.

The compounds of lithium with oxygen, iodine, bromine, and chlorine are the most suitable for the purpose; still the carbonate, sulphate, and even the phosphate give almost as distinct a reaction. Minerals containing lithium, such as triphylline, triphane, petalite, lepidolite, require only to be held in the flame in order to obtain the bright line Li *a* in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly shown, as, for instance, in the orthoclase from Baveno. The line is seen for a few moments only, directly after the mineral is brought into the flame. In the same way, the mica from Altenberg and Penig was found to contain lithium, whereas micas from Miask, Ashaffenburg, Modum, Bengal, Pennsylvania, &c., were found to be free from this metal. In natural silicates which contain only small traces of lithium, this metal is not observed so readily. The examination is then best conducted as follows:—A small portion of the substance is digested and evaporated with hydrofluoric acid or fluoride of ammonium, the residue moistened with sulphuric acid and heated, the dry mass being dissolved in absolute alcohol. The alcoholic extract is then evaporated, the dry mass again dissolved in alcohol, and the extract allowed to evaporate on a shallow glass dish. The solid pellicle which remains is scraped off with a fine knife, and brought into the flame upon the thin platinum wire. For one experiment, $\frac{1}{10}$ of a milligramme is in general quite a sufficient quantity. Other compounds besides the silicates, in which small traces of lithium require to be detected, are transformed into sulphates by evaporation with sulphuric acid or otherwise, and then treated in the manner described.

In this way we arrive at the unexpected conclusion, that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in 40 cubic centimetres of the water of the Atlantic Ocean, collected in 41° 41′ N. latitude, and 39° 14′ W. longitude. Ashes of marine plants (kelp), driven by the Gulf-stream on the Scotch coasts, contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contain lithium. A very pure spring water from the granite in Schlierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a litre of which lithium could hardly be detected by the ordinary methods of analysis, gave plainly the line Li *a*, even if only a drop of the water on a platinum wire was brought into the flame.* All the ashes of plants growing in the Odenwald on a granite soil, as well as Russian and other potashes, contain lithium. It was found also in the ashes of tabacco, of vine leaves, of the wood of the vine, and of grapes,† as well as in the ashes of the crops grown in the Rhine-plain near Waghäusel, Deidesheim, and Heidelberg, on a non-granitic soil. The milk of the animals fed upon these crops also contains lithium.‡

It is scarcely necessary to say that a mixture of volatile sodium and lithium salts gives the reaction of lithium alongside that of sodium with a scarcely perceptible diminution of precision and distinctness. The red lines of the former substance are still plainly seen when the bead contains $\frac{1}{1000}$ part of lithium salt, and when to the naked eye the yellow soda-flame appears untinged by the slightest trace of red. In consequence of the somewhat greater volatility of the lithium salt, the sodium reaction lasts longer than that of the other metal. In those cases, therefore, in which small quantities of lithium have to be detected in presence of large quantities of sodium, the bead must be brought into the flame whilst the observer is looking through the telescope. The lithium lines are often seen only for a few moments amongst the first products of the volatilization.

In the production of lithium salts on the large scale, in the proper choice of a raw material, and in the arrangement of suitable methods of separation, this spectrum-analysis affords most valuable aid. Thus it is only necessary to place a drop of mother-liquor from any mineral spring in the flame and to observe the spectrum produced, in order to show that in many of these waste products a rich and hitherto unheeded source of lithium salts exists. In the same way, during the course of the preparation, any loss of lithium in the collateral products and residues can be easily traced, and thus more convenient and economical methods of preparation may be found to replace those at present employed.§

Potassium.

Volatile potassium compounds give, when placed in the flame, a widely extended continuous spectrum, which contains only two characteristic lines, namely one line, Ka *a*, in the outermost red approaching the ultra-red rays, exactly coinciding with the dark line A of the solar spectrum, and a second line, Ka β, situated far in the violet rays towards the other end of the spectrum, and also identical with a particular dark line observed by Fraunhofer. A very indistinct line coinciding with Fraunhofer's line B, which, however, is seen only when the light is very intense, is not by any means so characteristic. The violet line is somewhat pale, but can be used almost as well as the red line for the detection of potassium. Owing to the position of these two lines, both situated near the limit at which our eyes cease to be sensitive to the rays, this reaction for potassium is not so delicate as the reaction for the two metals already mentioned. It became visible in the air of our room when one gramme of chlorate of potassium mixed with milk-sugar was burnt. In this way, therefore, the eye requires the presence of $\frac{1}{1000}$ of a milligramme of chlorate of potassium in order to detect the presence of potassium.

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* When liquids have to be brought into the flame, it is best to bend the end of the platinum wire, of the thickness of a horsehair, to a small ring, and to beat this ring flat. If a drop of liquid be brought into this ring, enough adheres to the wire for the experiment.

† In the manufactories of tartaric acid, the mother-liquors contain so much lithium salts that considerable quantities can thus be prepared.

‡ Dr. Folwarczny has been able, by help of the line Li *α*, to detect lithium in the ash of human blood and of muscular tissue.

§ We obtain by such an improved method from two jars (about 4 litres) of a mother-liquor from a mineral spring, which by evaporation with sulphuric acid gave $1^{k}\cdot2$ of residue, half an ounce of carbonate of lithium of the purity of the commercial, the cost of which is about 140 florins the pound. A great number of other mineral-spring mother-liquors which we examined showed a similar richness in compounds of lithium.

Caustic potash, and all compounds of potassium with volatile acids, give the reaction without exception. Potash silicates, and other non-volatile salts, on the other hand, do not produce the reaction by themselves, unless the metal is present in very considerable quantity; when, however, the amount of potassium is smaller, it is merely necessary to melt the substance with a bead of carbonate of sodium. The presence of the sodium does not in the least interfere with the reaction, and scarcely diminishes its delicacy. Orthoclase, sanidine, and adularia may in this way be easily distinguished from albite, oligoclase, Labradorite, and anorthite. In order to detect the smallest traces of potassium salt, the silicate requires only to be slightly ignited with a large excess of fluoride of ammonium on a platinum capsule, after which the residue is brought into the flame on a platinum wire. In this way, it is found that almost every silicate contains potassium. Salts of lithium diminish or influence the reaction as little as sodium salts. Thus we need only to hold the end of a burnt cigar in the flame before the slit, in order at once to see the yellow line of sodium and the two red lines of potassium and lithium, this latter metal being scarcely ever absent in tobacco ash.

Strontium.

The spectra produced by the alkaline earths are by no means so simple as those produced by the alkalies. That of strontium is especially characterized by the absence of green bands. Eight lines in the strontium-spectrum are remarkable, namely, six red, one orange, and one blue line. The orange line, Sr α, which appears close by the sodium line towards the red end of the spectrum, the two red lines, Sr β and Sr γ, and lastly, the blue line, Sr δ, are the most important strontium bands, both as regards their position and their intensity. To examine the intensity of the reaction, we quickly heated an aqueous solution of chloride of strontium, of known concentration, in a platinum dish over a large flame till the water was evaporated and the basin became red-hot. The salt then began to decrepitate, and was thrown up into the air, in microscopic particles in the form of a white cloud. On weighing the residual salt, it was found that in this way 0·077 grm. of chloride of strontium had been mixed in the form of a fine dust with the air of the room, weighing 77000 grms. As soon as the air in the room was perfectly mixed, by rapidly moving an open umbrella, the characteristic lines of the strontium-spectrum were beautifully seen. According to this experiment, a quantity of strontium may be thus detected equal to the $\frac{6}{100,000}$ part of a milligramme in weight.

The chloride and the other haloid salts of strontium give the best reaction. The hydrate and carbonate of strontium give it much less vividly, the sulphate still less, whilst the compounds of strontium with the non-volatile acids give either a very slight reaction or none at all. Hence it is well first to bring the bead of substance alone into the flame, and then again after moistening with hydrochloric acid. If it be supposed that sulphuric acid is present in the bead, it must be held in the reducing part of the flame before it is moistened with hydrochloric acid, for the purpose of changing the sulphate into the sulphide, which is decomposed by hydrochloric acid. To detect strontium when combined with silicic, phosphoric, boracic, and other non-volatile acids, it is best to proceed as follows:—Instead of fusing with carbonate of sodium in a platinum crucible, a conical spiral of platinum wire is employed; this spiral is heated to whiteness in the flame, and dipped while hot into finely-powdered dried carbonate of sodium which should contain so much water that a sufficient quantity adheres to the wire when it is once dipped into the salt. The fusion takes place in this spiral much more quickly than in a platinum crucible, as the mass of platinum requiring heating is small, and the flame comes into direct contact with the salt. As soon as the finely-powdered mineral has been brought into the fused soda by means of a small platinum spatula, and the mass retained above the melting point for a few minutes, the cooled mass has only to be turned upside down, and knocked on the porcelain plate of the lamp in order to obtain the salt in a large coherent bead. The fused mass is covered with a piece of writing paper, and then broken by pressing it with the blade of a steel spatula until the whole is reduced to a fine powder. The powder is brought to one spot on the edge of the plate, and carefully covered with hot water, which is allowed to flow backwards and forwards over it, so that, after decanting and rewashing the powder several times, all the soluble salts are extracted without losing any of the residue. If a solution of chloride of sodium be employed instead of water, the operation may be conducted more rapidly and with greater security. The insoluble salt contains the strontium as carbonate; and one or two tenths of a milligramme of the substance, brought on to the wire and moistened with hydrochloric acid, is sufficient to produce the most intense reaction. It is thus possible, without help of platinum crucible, mortar, evaporating basin, or funnel and filter, to fuse, powder, digest, and wash out the substance in the space of a few minutes.

The reactions of potassium and sodium are not influenced by the presence of strontium. Lithium also can be easily detected in presence of strontium when the proportion of the former metal is not very small. The lithium line Li *a* appears as an intensely red sharply defined band upon a less distinct red ground of the broad strontium band Sr β.

Calcium.

The spectrum produced by calcium is immediately distinguished from the four spectra already considered by the very characteristic bright green line Ca β. A second no less characteristic feature in the calcium spectrum is the intensely bright orange line Ca *a*, lying considerably nearer to the red end of the spectrum than either the sodium line Na *a*, or the orange band of strontium Sr *a*. By burning a mixture consisting of chloride of calcium, chlorate of potassium, and milk-sugar, a white cloud is obtained which gives the reaction with as great a degree of delicacy as strontium salts do under similar circumstances. In this way it was found that $\frac{6}{10,000,000}$ of a milligramme in weight of chloride of calcium can be detected with certainty. Only the volatile compounds of calcium give this reaction; the more volatile the salt, the more distinct and delicate does the reaction become. The chloride, bromide, and iodide of calcium are in this respect the best compounds. Sulphate of calcium does not produce the spectrum till it has become basic, but then very brightly and continuously. In the same way the reaction of the carbonate becomes more distinctly visible after the carbonic acid has been expelled.

Compounds of calcium with the non-volatile acids remain inactive in the flame; but if they are attacked by hydrochloric acid, the reaction may easily be obtained as follows: A few milligrammes of the finely powdered substance are placed on the moistened flat platinum ring in the moderately hot portion of the flame, so that the powder is fritted, but not melted on to the wire; if a drop of hydrochloric acid be now allowed to fall into the ring, so that the greater part of the acid remains hanging to the wire, and if the wire be then brought into the hottest part of the flame, the drop evaporates in the spheroidal state without ebullition. If the spectrum of the flame be observed during this operation, it will be noticed that at the moment when the last particles of liquid evaporate, a bright calcium spectrum appears. If the quantities of the metal present are very small, the characteristic lines are seen for a moment only; if larger quantities are contained, the phenomenon lasts for a longer time.

It is only in silicates which are decomposed by hydrochloric acid that the calcium can be thus detected. In those minerals which are not attacked by that acid, the examination is best made as follows. A few milligrammes of the substance under examination, in a state of fine division, are placed upon a flat platinum lid, together with about a gramme of fluoride of ammonium, and the mixture is gently ignited until all the fluoride is volatilized. The slight crust of salt remaining is moistened with a few drops of sulphuric acid, and the excess of acid removed by heat. If about a milligramme of the residual sulphates be scraped together with a knife, and brought into the flame, the characteristic spectra of potassium, sodium, and lithium, supposing these three metals to be present, are first obtained either simultaneously or consecutively. If calcium and strontium be also present, the corresponding spectra generally appear somewhat later, after the potassium, sodium, and lithium have been volatilized. When only traces of strontium and calcium are present, the reaction is not always seen; it becomes, however, immediately apparent on holding the bead for a few moments in the reducing flame, then moistening it with hydrochloric acid, and again bringing it into the flame.

These easy experiments, such as either heating the specimen alone, or after moistening with hydrochloric acid, or after treating the powder with fluoride of ammonium, either alone or in presence of sulphuric or hydrochloric acid, provide the mineralogist and geologist with a series of most simple methods of recognizing the components of the smallest fragment of many substances (such, for instance, as the double silicates containing lime) with a certainty which is attained in an ordinary analysis only by a large expenditure of time and material. The following examples will illustrate this statement.

1. A drop of sea-water heated on the platinum wire shows at first a strong sodium reaction; and after volatilization of the chloride of sodium, a weak calcium spectrum is observed, which on moistening the wire with hydrochloric acid becomes at once very distinct. If a few decigrammes of the residual salts obtained by the evaporation of sea-water be treated in the manner described under lithium with sulphuric acid and alcohol, the potassium and lithium reactions are obtained. The presence of strontium in sea-water can be best detected in the boiler-crust from sea-going steamers. The filtered hydrochloric acid solution of such a crust leaves, on evaporation and subsequent treatment with a small quantity of alcohol, a residue slightly yellow-coloured from basic iron salt, which is deposited after some days, and can then be collected on a small filter and washed with alcohol. The filter, burnt on a fine platinum wire and held in the flame, gives, besides the calcium lines, an intensely bright strontium spectrum.

2. Mineral waters often exhibit the reactions of potassium, sodium, lithium, calcium, and strontium by mere heating. If, for example, a drop of the Dürkheim or Kreuznach water be brought into the flame, the lines Na *α*, Li *α*, Ca *α*, and Ca *β* are at once seen. If, instead of using the water itself, a drop of the mother-liquor be taken, these bands appear most vividly. As soon as the chlorides of sodium and lithium have been to a certain extent volatilized, and the chloride of calcium has become more basic, the characteristic lines of the strontium spectrum begin to show themselves, and continue to increase in distinctness, until at last they come out in all their true brightness. In this case, therefore, by the mere observation of a single drop undergoing vaporization, the complete analysis of a mixture containing five constituents is performed in a few seconds.

3. The ash of a cigar moistened with hydrochloric acid, and held in the flame, shows at once the bands Na *α*, Ka *α*, Li *α*, Ca *α*, Ca *β*.

4. A piece of hard potash-glass combustion tubing gave, both with and without hydrochloric acid, the lines Na *α* and Ka *α*; treated with fluoride of ammonium and sulphuric acid, the bands Ca *α*, Ca *β*, and traces of Li *α* were rendered visible.

5. Orthoclase from Baveno gives, either alone or when treated with hydrochloric acid, only the line Na *α* with traces of Li *α* and Ka *α*; with fluoride of ammonium and sulphuric acid, the bright lines Na *α* and Ka *α*, and a somewhat less distinct Li *α*, are seen. After volatilization of the bodies thus detected, the bead moistened with hydrochloric acid gives a scarcely distinguishable flash of the lines Ca *α* and Ca *β*. The residue on the platinum wire, when moistened with cobalt solution and heated, gives the blue colour so characteristic of alumina. If the well-known reaction of silicic acid be likewise observed, we may conclude from this examination, made in the course of a very few minutes, that the orthoclase from Baveno contains silicic acid, alumina, potash with traces of soda, lime, and lithia; and also that no trace of baryta or strontia is present.

6. Adularia from St. Gothard comported itself in a similar manner, excepting that the calcium reaction was indistinctly seen, whilst that of lithium was altogether wanting.

7. Labradorite from St. Paul gives the sodium line Na *α*, but no calcium spectrum. On moistening the fragment with hydrochloric acid, the lines Ca *α* and Ca *β* appear very distinct; with the fluoride of ammonium test, a weak potassium reaction is obtained, and also faint indications of lithium.

8. Labradorite from the Corsican diorite gave similar reactions, except that no lithium was found.

9. Mosanderite from Brevig, and Tscheffkinite from the Ilmengebirge, showed, when treated alone, the sodium reaction; on the addition of hydrochloric acid, the lines Ca *α* and Ca *β*.

10. Melinophane from Lamoe gave the line Na *a* when placed alone in the flame; with hydrochloric acid, the lines Ca *a*, Ca *β*, and Li *a* became visible.

11. Scheelite and sphene, give on treatment with hydrochloric acid, a very intense calcium reaction.

12. When small quantities of strontium are present together with calcium, the line Sr δ may be most conveniently employed for the detection of this metal. In this way the presence of small quantities of strontium may be easily detected in very many sedimentary limestones. The lines Na *a*, Li *a*, Ka *a*, especially Li *a*, are observed as soon as the limestone is brought into the flame. Converted by hydrochloric acid into chlorides, and brought in this form into the flame, these minerals give the same bands; and not unfrequently the line Sr δ is also distinctly seen. This latter appears, however, only for a short time, and is in general best seen when the calcium spectrum begins to fade.

In this way, the lines Na *a*, Li *a*, Ka *a*, Ca *a*, Ca *β*, and Sr δ were found in the spectra of the following limestones:—

Limestone from the Silurian at Kugelbad near Prague. Muschelkalk from Rohrbach near Heidelberg. Limestone from the Lias at Malsch in Baden. Chalk from England.

The following limestones gave the lines Na *a*, Li *a*, Ka *a*, Ca *a*, Ca *β*, but not the blue strontium band Sr δ:—

Marble from the granite near Auerbach.* Devonian limestone from Gerolstein in the Eifel. Carboniferous limestone from Planitz in Saxony. Dolomite from Nordhausen in the Harz. Jura-kalk from Streitberg in Franconia.

From these few experiments, it is evident that a more extended series of exact spectrum analyses, respecting the amount of strontium, lithium, sodium, and potassium which the various limestone formations contain, must prove of the greatest geological importance, both as regards the order of their formation and their local distribution, and may possibly lead to the establishment of some unexpected conclusions respecting the nature of the oceans from which these limestones were originally deposited.

Barium.

The barium spectrum is the most complicated of the spectra of the alkalies and alkaline earths. It is at once distinguished from all the others by the green lines Ba *a* and Ba *β* (which are by far the most distinct) appearing the first and continuing during the whole of the reaction. Ba γ is not quite so distinct, but is still a well-marked and peculiar line. As the barium spectrum is considerably more extended than those of the other metals, the reaction is not observed to so great a degree of delicacy; still

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* According to the method already described, a quantity of nitrate of strontium was obtained from 20 grms. of this marble such as to give a complete and vivid strontium spectrum. We have not examined the other limestones in the same way.

0·3 grm. of chlorate of barium burnt with milk-sugar gave a distinct band of Ba *a* which lasted for some time, when the air of the room was well mixed by moving an open umbrella about. Hence we may calculate, in the same manner as was done in the sodium experiment, that about $\frac{1}{1000}$ of a milligramme of barium salt may be detected with certainty.

The chloride, bromide, iodide, and fluoride, of barium, as also the hydrate, the sulphate, and carbonate, show the reaction best. It may be obtained by simply heating any of these salts in the flame.

Silicates containing barium, which are decomposed by hydrochloric acid, also give the reaction if a drop of hydrochloric acid be added to them before they are brought into the flame. Baryta-harmotome, treated in this way, gives the lines Ca *a* and Ca *β*, together with the bands Ba *a* and Ba *β*.

Compounds of barium with fixed acids, giving no reaction either when alone or after addition of hydrochloric acid, should be fused with carbonate of sodium, as described under strontium, and the carbonate of barium thus obtained, examined. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid, and the dried salt extracted with alcohol. The residue contains only barium and strontium, both of which can almost always be detected. When we wish to test for small traces of strontium or barium, the residual nitrates are converted into chlorides by ignition with sal-ammoniac, and the chloride of strontium is extracted by alcohol. Unless the quantity of one or more of the bodies to be detected is extremely small, the methods of separation just described are quite unnecessary, as is seen from the following experiment:—

A mixture of the chlorides of potassium, sodium, lithium, calcium, strontium, and barium, containing at the most $\frac{1}{10}$ of a milligramme of each of these salts, was brought into the flame, and the spectra produced were observed. At first the bright yellow sodium line Na *a* appeared, with a background formed by a nearly continuous pale spectrum. As soon as this line began to fade, the exactly defined bright red line of Lithium Li *a* was seen; and beyond this, still farther from the sodium line, the faint red potassium line Ka *a* was noticed, whilst the two barium lines, Ba *a*, Ba *β*, with their peculiar shading, became distinctly visible in their characteristic places. As the potassium, sodium, lithium, and barium salts volatilized, their spectra became fainter and fainter, and their peculiar bands one after the other vanished, until, after the lapse of a few minutes, the lines Ca *a*, Ca *β*, Sr *a*, Sr *β*, Sr *γ*, and Sr *δ*, became gradually visible, and like a dissolving view, at last attained their characteristic distinctness, colouring, and position, and then after some time, became pale and disappeared entirely.

The absence of any one or of several of these bodies is at once indicated by the non-appearance of the corresponding bright lines.

Those who become acquainted with the various spectra by repeated observation, do not need to have before them an exact measurement of the individual lines in order to be able to detect the presence of the various constituents; the colour, relative position, peculiar form, variety of shade and brightness of the bands are quite characteristic enough to ensure exact results, even in the hands of persons unaccustomed to such work. These special distinctions may be compared with the differences of outward appearance presented by the various precipitates employed for detecting substances in the wet way. Just as a precipitate is characterized as gelatinous, pulverulent, flocculent, granular, or crystalline, so the lines of the spectrum exhibit their peculiar aspects, some appearing sharply defined at their edges, others blended off either at one or both sides, either similarly or dissimilarly, some, again, appearing broader, others narrower; and just as in ordinary analysis we make use of those precipitates only which are produced with the smallest possible quantity of the substance supposed to be present, so in analysis with the spectrum, we employ only those lines which are produced by the smallest possible quantity of substance and require a moderately high temperature. In these respects, both analytical methods stand on an equal footing; but analysis with the spectrum possesses a great advantage over all other methods, inasmuch as the characteristic differences of colour of the lines serve as the distinguishing feature of the system. Most of the precipitates which are valuable as reactions are colourless; and the tint of those which are coloured varies very considerably according to the state of division and mechanical arrangement of the particles. The presence of even the smallest quantity of impurity is often sufficient entirely to destroy the characteristic colour of a precipitate; so that no reliance can be placed upon nice distinctions of colour as an ordinary chemical test. In spectrum-analysis, on the contrary, the coloured bands are unaffected by such alteration of physical conditions, or by the presence of other bodies. The positions which the lines occupy in the spectrum indicate the existence of a chemical property as unalterable as the combining weights themselves, and may therefore be estimated with almost astronomical precision. The fact, however, which gives to this method of spectrum-analysis a peculiar degree of importance is, that it extends almost to infinity, the limits within which the chemical characteristics of matter have been hitherto confined. By an application of this method to geological inquiries concerning the distribution and arrangement of the components of the various formations, the most valuable results may be expected; even the few random experiments already mentioned have led to the unexpected conclusion, that not only potassium and sodium, but also lithium and strontium must be added to the list of bodies occurring, only indeed in small quantities, but most widely spread, throughout the matter composing the solid body of our planet.

The method of spectrum-analysis may also play a no less important part as a means of detecting new elementary substances; for if bodies should exist in nature so sparingly diffused that the analytical methods hitherto applicable have not succeeded in detecting or separating them, it is very possible that their presence may be revealed by a simple examination of the spectra produced by their flames. We have had opportunity of satisfying ourselves that in reality such unknown elements exist. We believe that, relying upon unmistakeable results of the spectrum-analysis, we are already justified in positively stating that, besides potassium, sodium, and lithium, the group of the alkaline metals contains a fourth member, which gives a spectrum as simple and characteristic as that of lithium—a metal which in our apparatus gives only two lines, namely a faint blue one, almost coincident with the strontium line Sr δ, and a second blue one lying a little further towards the violet end of the spectrum, and rivalling the lithium line in brightness and distinctness of outline.

The method of spectrum-analysis not only offers, as we think we have shown, a mode of detecting with the greatest simplicity the presence of the smallest traces of certain elements in terrestrial matter, but it also opens out the investigation of an entirely untrodden field, stretching far beyond the limits of the earth, or even of our solar system. For, in order to examine the composition of luminous gas, we require, according to this method, only to see it; and it is evident that the same mode of analysis must be applicable to the atmospheres of the sun and of the brighter fixed stars. A modification must, however, be introduced on account of the light emitted by the solid nuclei of these heavenly bodies. In a Memoir published by one of us,* "On the relation between the Coefficients of Emission and Absorption of Bodies for Heat and Light," it was proved from theoretical considerations that the spectrum of an incandescent gas becomes *reversed* (that is, that the bright lines become changed into dark ones) when a source of light of sufficient intensity, giving a continuous spectrum, is placed behind the luminous gas. From this we may conclude that the solar spectrum, with its dark lines, is nothing else than the reverse of the spectrum which the sun's atmosphere alone would produce. Hence, in order to effect the chemical analysis of the solar atmosphere, all that we require is to discover those substances which, when brought into the flame, produce bright lines coinciding with the dark ones of the solar spectrum.

In the paper above referred to, the following experimental facts are given in confirmation of the preceding theoretical conclusion.

The bright red line produced in the spectrum of a gas-flame by the presence of a bead of chloride of lithium, is changed into a dark one when direct sunlight is allowed to pass through the flame. When the bead of lithium is replaced by one of chloride of sodium, the dark double line D (coincident with the yellow sodium line) appears with uncommon distinctness. The dark double line D also appears when the rays of a Drummond's light are passed through the flame of aqueous alcohol into which chloride of sodium is thrown.†

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* Kirchhoff, Poggendorff's Annalen, cix. 275; and Phil. Mag. [4], xx. 1.

† In the Philosophical Magazine for March 1860, Prof. Stokes calls attention to the fact that in the year 1849, Foucault made an observation very similar to the above. In the examination of the spectrum produced by the electric arc between carbon points, Foucault noticed that bright lines occur where the double line D of the solar spectrum is found, and that this dark line D is produced or made more intense when the rays of the sun, or those from one of the incandescent carbon poles, are passed through the luminous arc. The observation mentioned in the text affords

It appeared of interest to obtain still further confirmation of this important theoretical conclusion; the following experiments answered this purpose:—

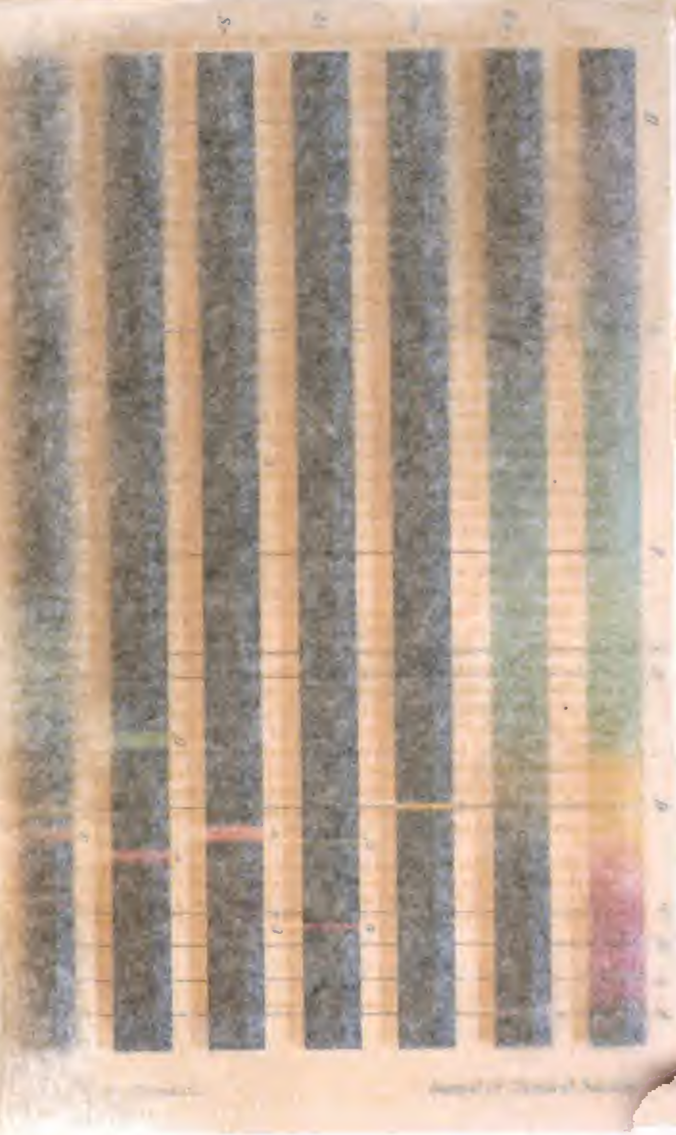
We ignited a thick platinum wire in the flame, and then by means of an electric current, heated it to a temperature approaching its melting-point. The wire gave a bright spectrum, in which no trace of either dark or bright lines was seen. A flame of weak aqueous alcohol, in which common salt was dissolved, on being brought between the wire and the slit of the apparatus, gave the dark line D most distinctly.

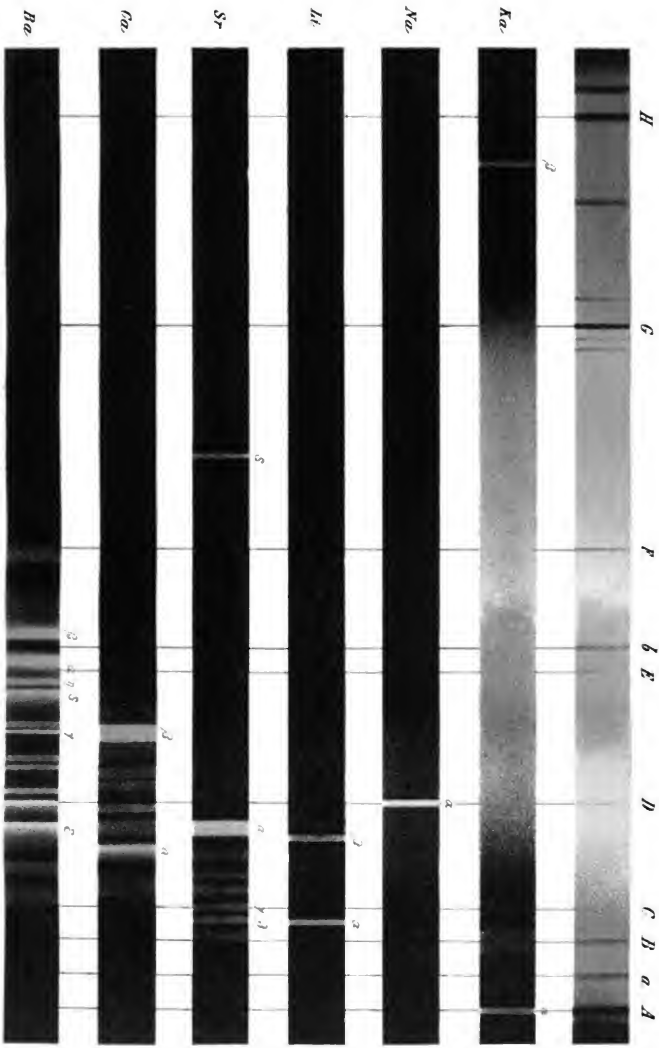
The dark line D can be produced in the spectrum of a platinum wire heated in a flame, by holding between flame and spectrum a test-tube containing some sodium amalgam which is heated to boiling.

This experiment is important, because it shows that sodium vapour at a temperature much below that at which it becomes luminous, exerts its absorptive power at exactly the same point of the spectrum as it does at the highest temperatures which we can produce, or at the temperatures existing in the solar atmosphere.

We have succeeded in reversing the bright lines in the spectra of K, Sr, Ca, Ba, by employing sunlight and mixtures of the chlorates of these metals with milk-sugar. A small iron trough was fixed in front of the slit of our apparatus, in which the mixture was placed; the direct sunlight was then allowed to pass along the whole length of the trough, and the mixture was ignited with a heated wire. The telescope C, with the wires cutting each other at an oblique angle, was placed so that the point of intersection of the wires coincided with the bright line of the flame-spectrum which was to be examined. The observer concentrated his attention upon this point, to judge whether, at the moment of burning the mixture, a dark line showed itself passing through the point of intersection of the cross wires. In this way it was easy, when the right proportions for the mixtures were found, to show that the lines Ba α, Ba β, as well as the line Ka β, were reversed. The last of these lines coincides with one of the most distinct dark lines in the solar spectrum, though not marked by Fraunhofer, which, however, appears much more plainly than it is generally seen at the moment the potash salt burns. In order to prove that the strontium lines can be reversed, the chlorate of strontium must be most carefully dried, as the slightest trace of moisture produces a positive strontium spectrum, owing to small particles of salt being thrown about in the flame, and thus diminishing the power of the solar rays.

an explanation of this interesting phænomenon observed by Foucault eleven years ago, proving that it is not occasioned by the properties of the electric light, which in many respects is still so enigmatical, but that it arises from a compound of sodium contained in the pole, and converted into incandescent gas by the current.





M & N Hanhart, Chromolith

Journal of Chemical Society.

	Calculated.	Found.	
	$C_9H_8BaNO_3 + 1\frac{1}{2}H_2O$		
Water of crystallization . .	9·87	9·61	10·11

Acetoxybenzamate of calcium, $C_9H_8CaNO_3 + 1\frac{1}{2}H_2O$.—This salt was prepared by saturating the acid with milk of lime and removing the excess of lime by carbonic acid. It is only moderately soluble in cold water, and can be easily obtained in well-defined crystals, consisting of very thin rhombic plates, by cooling its hot aqueous solution.

·6428 grm., air-dry, lost ·081 grm. water at 130°.
·63 grm. lost ·0781 grm. water at 130°.
·2978 grm., dried at 130°, gave ·1039 grm. sulphate of calcium.
·2087 grm. gave ·0722 grm. sulphate of calcium.
·342 grm., burned with chromate of lead, gave ·6786 grm. carbonic acid, and ·1337 grm. water.

		Calculated.	Found.		
C_9	108	54·55	—	—	54·12
H_8	8	4·04	—	—	4·34
Ca	20	10·10	10·26	10·17	—
N	14	7·07	—	—	—
O_3	48	24·24	—	—	—
$C_9H_8CaNO_3$	198	100·00			

	Calculated.	Found.	
	$C_9H_8CaNO_3 + 1\frac{1}{2}H_2O$		
Water of crystallization . . .	12·0	12·6	12·4

Acetate of *lead* gives, with a solution of an acetoxybenzamate, a sticky precipitate which melts in boiling water and gradually dissolves; it is also soluble in alcohol.

Nitrate of *silver* and chloride of *zinc*, give no precipitate with a moderately strong solution of an acetoxybenzamate. With a concentrated solution, nitrate of silver gives a precipitate which blackens on boiling.

Acetoxybenzamate of ethyl.—This substance cannot be obtained by the process indicated by Stenhouse for the preparation of hippurate of ethyl, namely, by heating the acid with alcohol saturated with hydrochloric acid. The manner in which acetoxybenzamic acid is decomposed under these circumstances has already been described. When acetoxybenzamic acid and absolute alcohol are heated together, no apparent action takes place at 100°; but at about 150° a compound is formed which is soluble in ether and can thus be separated from the acid which remains in excess. This body, which is probably acetoxybenzamate of ethyl, is very slightly soluble in cold water, but tolerably soluble in hot water; from this solution it sometimes separates, by cooling, in the form of an oil which solidifies gradually on standing. If long boiled with water it regenerates acetoxybenzamic acid. It is very soluble in alcohol. On heating this substance to 100° in a Liebig's drying-tube, in order to dry it for analysis, a few drops of a colourless liquid which was scarcely soluble in water but miscible with alcohol, and which greatly resembled carbolic acid in taste and smell, condensed in the tube leading to the aspirator. As this liquid continued slowly to distil after the substance had been heated for many hours to 100°, the temperature was raised to between 130° and 135°. At this temperature the liquid distilled more rapidly and was accompanied by a crystalline sublimate; at the same time the supposed acetoxybenzamate of ethyl rapidly became of a dark brown colour. Neither the liquid nor the sublimate was obtained in sufficient quantity for further examination.

Cahours* mentions a substance which he obtained by the action of chloride of benzoyl on oxybenzamate of silver, but of which he neither gives the formula nor describes the properties. Hoping to obtain benzoyl-oxybenzamic acid, I reacted on oxybenzamate of zinc with chloride of benzoyl. The product was an acid insoluble in cold water and in ether, slightly soluble in boiling water, in alcohol, and in chloroform, and resembling acetoxybenzamic acid in taste and in its appearance under the microscope. A determination of nitrogen by Dumas's process and the mean of two concordant combustions gave the following results:—

Carbon	68·03
Hydrogen	5·12
Nitrogen	6·27
Oxygen	20·58
	100·00

which differ too much from the calculated composition of benzoyl-oxybenzamic acid; namely—

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* Ann. Ch. Pharm., ciii. 90. This product is spoken of as glycobenzamic acid in the Handwörterbuch.

Carbon	69·71
Hydrogen	4·56
Nitrogen	5·81
Oxygen	19·92
	100·00

It is a matter of some interest to consider the relation in which acetoxybenzamic acid stands to hippuric acid, and the nature of the isomerism of these two bodies.

If we bear in mind the close analogy which exists between glycocol and oxybenzamic acid, the formation of acetoxybenzamic acid from chloride of acetyl and oxybenzamate of zinc is strictly comparable to the formation of hippuric acid from chloride of benzoyl and zinc-glycocol; and its decomposition, when heated with water in presence of a strong acid, into acetic and oxybenzamic acids is analogous to the decomposition of hippuric acid into benzoic acid and glycocol.

$$\left\{\begin{array}{l} \underset{\text{Chloride of acetyl.}}{C_2H_3OCl} + \underset{\text{Oxybenzamate of zinc.}}{C_7H_6ZnNO_2} = \underset{\text{Acetoxybenzamic acid.}}{C_9H_9N_3O} + ZnCl \\ \\ \underset{\text{Chloride of benzoyl.}}{C_7H_5OCl} + \underset{\text{Zinc-glycocol.}}{C_2H_4ZnNO_2} = \underset{\text{Hippuric acid.}}{C_9H_9NO_3} + ZnCl \end{array}\right.$$

$$\left\{\begin{array}{l} \underset{\text{Acetoxybenzamic acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Oxybenzamic acid.}}{C_7H_7NO_2} \\ \\ \underset{\text{Hippuric acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Glycocol.}}{C_2H_5NO_2} \end{array}\right.$$

Allowing for the difference between acetyl and benzoyl, acetoxybenzamic acid is to oxybenzamic acid what hippuric acid is to glycocol. The simplest way of expressing these relations in the formulæ of the two substances is to write acetoxybenzamic acid as an acetyl-derivative of oxybenzamic acid (or as oxybenzamic acid in which an atom of hydrogen is replaced by acetyl), and hippuric acid as a benzoyl-derivative of glycocol (or as glycocol in which an atom of hydrogen is replaced by benzoyl).

Before we can give formulæ which will indicate the further relations of these acids, it is therefore necessary to consider the formulæ of glycocol and oxybenzamic acid. These two bodies occupy corresponding positions in two analogous series of compounds.

Acetic acid .	$C_2H_4O_2$	Benzoic acid .	$C_7H_6O_2$
Chloracetic acid	$C_2H_3ClO_2$	Nitrobenzoic acid	$C_7H_5(NO_2)O_2$
Glycocol . .	$C_2H_5NO_2$	Oxybenzamic acid	$C_7H_7NO_2$
Glycollic acid	$C_2H_4O_3$	Oxybenzoic acid	$C_7H_6O_3$

There are two principal points of view from which the members of the two series may be regarded, and accordingly two principal systems of rational formulæ by which they may be represented. We may, on the one hand, adopt formulæ expressing only the genetic relations of the two sets of compounds to acetic and benzoic acids respectively; or, on the other hand, formulæ which express in addition the general nature of the differences which the various terms of each series exhibit in their relation to other substances. In the first case, if we write acetic and benzoic acids as deriving from the type H_2O, we get—

Acetic Series.

Acetic acid	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$
Chloracetic acid . . .	$\left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O$
Glycocol.	$\left.\begin{matrix}C_2H_2(H_2N)\\H\end{matrix}\right\}O$
Glycollic acid	$\left.\begin{matrix}C_2H_2(HO)\\H\end{matrix}\right\}O$

Benzoic Series.

Benzoic acid	$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$
Nitrobenzoic acid . . .	$\left.\begin{matrix}C_7H_4(NO_2)O\\H\end{matrix}\right\}O$
Oxybenzamic acid . . .	$\left.\begin{matrix}C_7H_4(H_2N)O\\H\end{matrix}\right\}O$
Oxybenzoic acid . . .	$\left.\begin{matrix}C_7H_4(HO)O\\H\end{matrix}\right\}O$

In the second case we get the following, or equivalent formulæ:—

Acetic Series.

Type.

Acetic acid . . . $$\begin{array}{rl} H & \rbrace \\ C_2H_2O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Chloracetic acid . . $$\begin{array}{rl} Cl & \rbrace \\ C_2H_2O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} Cl & \rbrace \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Glycocol . . . . $$\begin{array}{rl} H & \rbrace \\ H & \rbrace\ N \\ C_2H_2O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace \\ H & \rbrace\ N \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Glycollic acid . . . $$\begin{array}{rl} H & \rbrace\ O \\ C_2H_2O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace\ O \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Benzoic Series.

Benzoic acid . . . $$\begin{array}{rl} H & \rbrace \\ C_7H_4O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

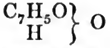
Nitrobenzoic acid . . $$\begin{array}{rl} NO_2 & \rbrace \\ C_7H_4O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} NO_2 & \rbrace \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Oxybenzamic acid . . $$\begin{array}{rl} H & \rbrace \\ H & \rbrace\ N \\ C_7H_4O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace \\ H & \rbrace\ N \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

Oxybenzoic acid . . $$\begin{array}{rl} H & \rbrace\ O \\ C_7H_4O & \rbrace \\ H & \rbrace\ O \end{array} \cdots \begin{array}{rl} H & \rbrace\ O \\ H & \rbrace \\ H & \rbrace \\ H & \rbrace\ O \end{array}$$

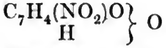
It will be seen that these two systems of formulæ differ in this: that, in the first set, the type remains unchanged throughout, but that the radicle is different in each compound; while, in the second set, the type is variable but the radicle constant. It may perhaps be said that this difference is not essential, but merely a difference of form: the elements which, in the one case, are represented as replacing hydrogen in the radicles acetyl and benzoyl and are written in the same line with the remaining elements of these radicles, being, in the other case, separated and written above the other elements. Admitting this to be the case, and supposing the two sets of formulæ to be used in the same sense, the question arises whether or no one set of formulæ is preferable to the other as a matter of form.

On this point it may be observed, first, that the only consistent definition of a compound radicle is *a group of elements contained in a greater or less number of substances and not altered by the reactions by which these substances are transformed one into another*, and that it is therefore inconsistent to represent closely allied and mutually convertible substances as containing different radicles; secondly, that the only consistent use of typical formulæ is *to express the nature of the transformations which the bodies represented by them are capable of undergoing*, and, therefore, that it is inconsistent to refer to the same type, bodies of which the transformations are very different. For example, the formulæ—



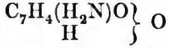
$$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$$

Benzoic acid,



$$\left.\begin{matrix}C_7H_4(NO_2)O\\H\end{matrix}\right\}O$$

Nitrobenzamic acid,

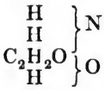


$$\left.\begin{matrix}C_7H_4(H_2N)O\\H\end{matrix}\right\}O$$

Oxybenzamic acid,

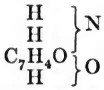
ought to imply that the salts of these three acids give similar products when acted upon by acid chlorides, such as chloride of acetyl or chloride of benzoyl: experiment, however, proves that the first two give anhydrides when so acted upon, while the third gives a well characterized acid. The same difference also exists between the salts of acetic acid and the salts of glycocol in respect to their behaviour with similar reagents.

For these reasons, the relations of glycocol and oxybenzamic acid to their congeners are most correctly expressed by the formulæ—



$$\begin{matrix}H\\H\\C_2H_2O\\H\end{matrix}\begin{matrix}\left.\vphantom{\begin{matrix}H\\H\end{matrix}}\right\}N\\\left.\vphantom{\begin{matrix}H\\H\end{matrix}}\right\}O\end{matrix}$$

and



$$\begin{matrix}H\\H\\C_7H_4O\\H\end{matrix}\begin{matrix}\left.\vphantom{\begin{matrix}H\\H\end{matrix}}\right\}N\\\left.\vphantom{\begin{matrix}H\\H\end{matrix}}\right\}O\end{matrix}$$

Glycocol. Oxybenzamic acid.

which represent them as amidic acids corresponding respectively to glycollic (oxyacetic) acid and oxybenzoic acid. Hence, for hippuric and acetoxybenzamic acids we get the formulæ—

$$\left.\begin{array}{c}\left.\begin{array}{c}H\\C_7H_5O\\(C_2H_2O)''\end{array}\right\}N\\\left.\begin{array}{c}\\H\end{array}\right\}O\end{array}\right. \quad \text{and} \quad \left.\begin{array}{c}\left.\begin{array}{c}H\\C_2H_3O\\(C_7H_4O)''\end{array}\right\}N\\\left.\begin{array}{c}\\H\end{array}\right\}O\end{array}\right.$$

Hippuric acid.
(Benzoyl-oxyacetamic acid.)

Acetyl-oxybenzamic acid.

By way of justification of this discussion of what may seem very obvious formulæ, I may perhaps be allowed to give a collection (probably far from complete) of formulæ which have recently been proposed for glycocol, hippuric acid, and oxybenzamic acid.

GLYCOCOL.	HIPPURIC ACID.	OXYBENZAMIC ACID.
$N\left\{\begin{array}{c}C_2H_3O_2\\H\\H\end{array}\right.$	$N\left\{\begin{array}{c}C_2H_3O_2\\C_7H_5O\\H\end{array}\right.$	
		Gerhardt, Traité iv, 767, (1856).
$C_4H_3(H_2N)O_4$		$C_{14}H_5(H_2N)O_4$
		Cahours, Ann. Ch. Phys., [3] liii, (1858).
$N\left\{\begin{array}{l}\left.\left\{\begin{array}{c}C_2\overset{\prime\prime}{H}_2O\\H\end{array}\right.\right\}O\\H_2\end{array}\right.$		$N\left\{\begin{array}{l}\left.\left\{\begin{array}{c}C_7H_4O\\H\end{array}\right.\right\}O\\H_2\end{array}\right.$
		Wislicenus, Zeitschr. f. d. gesammt. Naturwissenschaften, xiv, (1859).
$N\left\{\begin{array}{c}C_2HO_2\\C_2H_3\\H\end{array}\right\}\overset{*}{O}_2$	$N\left\{\begin{array}{c}C_2\ \overset{\prime\prime}{O}_2\\C_{14}H_5O_2\\C_2\ H_3\\H\end{array}\right\}\overset{*}{O}_2$	$\overset{\prime\prime}{N}\left\{\begin{array}{c}C_{14}H_5O_2\\H_2\end{array}\right\}\overset{*}{O}_2$
		Weltzien, Zusammenstell. d. organ. Verbind. (1860).
$\left.\begin{array}{c}C_4\overset{\prime}{\overparen{H_2(N}}\overset{\prime}{H}_2)O_2\\H\end{array}\right\}\overset{*}{O}_2$	$\left.\begin{array}{c}C_{14}H_4.(C_4\overset{\prime}{\overparen{H_2.N}}H_2.O_2)O_2\\H\end{array}\right\}\overset{*}{O}_2$	$\left.\begin{array}{c}C_{14}\overset{\prime}{\overparen{H_4(N}}H_2)O_2\\H\end{array}\right\}\overset{*}{O}_2$
		Gorup-Besanez, Lehrb. d. organ. Chemie, ii, (1860)
$HO.\left(C_2\left\{\begin{array}{c}H_2\\H_2N\end{array}\right.\right)[C_2\overset{*}{O}_2].O$	$HO.C_{12}\left\{\begin{array}{c}H_4\\\left(C_2\left\{\begin{array}{c}H_2\\H_2N\end{array}\right.\right)C_2O_2\end{array}\right\}[C_2\overset{*}{O}_2],O$	$HO.\left(C_{12}\left\{\begin{array}{c}H_4\\H_2N\end{array}\right.\right)[C_2O_2],O$
		Kolbe, Ann. Ch. Pharm., cxiii, (1860).
$\begin{array}{c}\left.\begin{array}{c}H\\H\\CO\end{array}\right\}N\\\left.\begin{array}{c}CH_2\\H\end{array}\right\}O\end{array}$	$\begin{array}{c}\left.\begin{array}{c}H\\C_7H_5O\\CO\end{array}\right\}N\\\left.\begin{array}{c}C\ H_2\\H\end{array}\right\}O\end{array}$	
		Limpricht, Lehrb. d. organ. Chemie, (1860).

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* In the formulæ marked with an asterisk, H = 1, C = 6, O = 8.

It is hardly necessary to add, in conclusion, that I make no claim to originality in reference to the formulæ proposed in this paper. Gerhardt, in the formula quoted above, represented hippuric acid as benzoyl-glycocol, and the formulæ which I have adopted for oxybenzamic acid and glycocol were first proposed by Kekulé (Ann. Ch. Pharm., civ. 148; cvi. 150). Moreover, the formulæ for glycocol and hippuric acid which are quoted from Limpricht are very nearly identical with those proposed in this paper. The only difference is, that in order to represent other reactions than those which are here taken into account, he has divided the radicle C_2H_2O into CO and CH_2, and has consequently derived glycocol and hippuric acid from the type $\left.\begin{matrix}H_5N\\H_2O\end{matrix}\right\}$, which might perhaps be more correctly written $\left.\begin{matrix}H_2\\H_3N\\H_2O\end{matrix}\right\}$; for though in some compounds nitrogen is combined with the equivalent of five atoms of hydrogen, these substances are always easily broken up into a group equivalent to H_2 and a group equivalent to H_3N.

Through the kindness of Professor Kekulé, of the University of Ghent, I have been able to perform the experiments described in this paper in his laboratory.

Ghent, 19th June, 1860.

XXI.—*On Baudrimont's Protosulphide of Carbon.*

By Lyon Playfair, C.B., F.R.S.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

Baudrimont has given various processes for the preparation of protosulphide of carbon, a body long expected by chemists and necessary to complete the analogy between sulphur and oxygen. Protosulphide of carbon bears the same analogy to carbonic oxide that bisulphide of carbon does to carbonic acid. The discovery of the body surprised no one, but it was a matter of astonishment that the numerous and simple processes for its preparation had remained so long unknown to chemists.

The description given by Baudrimont* for the preparation and properties of this interesting body is short, further details being promised in a future paper. Meanwhile, the new compound has received admission into systematic works on Chemistry.

Being desirous of making some experiments with protosulphide of carbon, I have repeated without success the processes described by Baudrimont; I have been equally unsuccessful with others which appeared equally promising. It is therefore desirable to obtain further evidence of this existence of the compound; for the products of the processes described are in most cases only carbonic oxide with the vapours of bisulphide of carbon, and, in other cases, mixtures of carbonic oxide, hydrogen, carburetted hydrogen and the vapours of bisulphide of carbon.

Baudrimont, in the memoir above referred to, gives nine processes for the preparation of protosulphide of carbon, but admits that only the first process yielded it in a state of tolerable purity. To this process it will therefore be sufficient to direct special attention. The vapours of bisulphide of carbon are to be passed over red hot pumice-stone or spongy platinum, which have the effect, according to Baudrimont, of doubling the compound, (so much sulphur being at the same time deposited as to choke the exit tubes), while the gaseous protosulphide of carbon passes on, and may be collected, after transmission through solutions of acetate of lead and dichloride of copper.

In repeating this and subsequent experiments, it became obvious that the presence of organic matter and moisture was a frequent source of error, and it was necessary to operate so as to exclude these; accordingly the following arrangement was adopted:—

A long tube of difficultly fusible glass was filled with fragments of pumice-stone to the extent of three feet in length, and then the posterior end was drawn out into a U shape, and the anterior end into a delivery tube for gaseous products. The capacity of the whole tube was about 95 cubic centimeters. The body of the tube containing the pumice stone was placed in Hofmann's gas furnace and heated, a stream of carbonic acid, dried by sulphuric acid, being passed over it until all moisture was expelled. When the desiccation of the tube and pumice-stone had been effected, 8 grammes of dry bisulphide of carbon were sucked into the U portion of the tube, which was then sealed by a lamp and placed in a water-bath.

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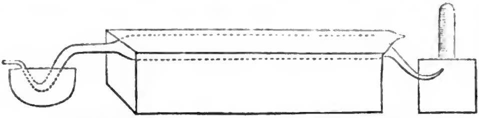
* Comptes rendus, xliv, 1000.

The whole of the bisulphide of carbon was now slowly passed over the red hot pumice and the products were collected over mercury by the delivery portion of the tube. The heat employed was sufficient to alter the shape of the tube, although it was protected as is usual in combustion, by metallic gauze.



During the experiment gas came over, and with it liquid bisulphide which condensed in the eudiometer. After the 8 grammes of bisulphide had been slowly passed over the red hot pumice-stone, the products were as follows:—

Gas at 730mm. press. 12°C. temp. . . .	155 cub. cent.
Liquid bisulphide of carbon	5 cub. cent.

The gas corrected for temp. and pressure, and for the tension of CS_2 with which it was saturated (200mm. at 12°C. Brezelius) gave

Corrected vol. of gas and 0°C. and 760mm. press. 103·5 cub. cent.

Caustic potash was now passed up to absorb carbonic acid and sulphuretted hydrogen, and the gas now measured 59 cub. cent. at 12°C. and 610mm. pressure, still saturated with bisulphide of carbon. Corrected for this and brought to the normal temperature and pressure there was only 30·49 cub. cent. of gas left.

Hence of the 8 grammes of bisulphide, at least 6·4 grammes were found condensed in the eudiometer; the remaining 1·6 gramme was chiefly in the long delivery tube, which had a column of condensed bisulphide in it, but this was not measured. If we neglect this and assume that 1·3 gramme was decomposed into protosulphide of carbon (0·3 gramme in vapour being allowed for the capacity of the tube), 383 cub. cent. of this gas should have been produced. But after correcting for the pressure, temperature, and for the tension of CS_2, only 30·49 cub. cent. were obtained. This small quantity of residual gas consisted of carbonic oxide and nitrogen, resulting from the traces of air and moisture still left in the pumice-stone, or introduced when the bisulphide of carbon was drawn into the apparatus. But if we assumed the whole residual gas to be protosulphide of carbon, it would have weighed only 0·060 gramme, and would have been produced from 0·09 gramme of the bisulphide. Hence in any case not more than 1·4 per cent. of the bisulphide employed could have been decomposed in its passage through the red-hot pumice. But this gas was chiefly carbonic oxide produced by the action of moisture—($CS_2 + HO = CO + S + HS$,) and required only 0·027 HO to produce it, a quantity which can easily have escaped the drying process.

A careful examination of the tube and pumice-stone showed that no sulphur whatever was deposited, except one or two specks which could not have been weighed, the whole operation having been one of simple distillation without decomposition. When the pumice-stone is not completely dry, then sulphuretted hydrogen and carbonic oxide appear, while sulphur is deposited.

Having failed in obtaining protosulphide of carbon by the only process which Baudrimont describes as giving it pure, it was scarcely necessary to repeat the other methods; but those described as yielding the best results were examined. The chief of these is to pass the vapours of bisulphide of carbon over red-hot charcoal, animal charcoal being recommended.

On repeating these experiments, large quantities of gas were obtained at first; but the gas ceased abruptly, although the tube still contained abundance of animal charcoal, and now bisulphide of carbon distilled over unchanged. The gas collected in the first part of the experiment was washed with solution of acetate of lead and dichloride of copper, but continually decreased in bulk, until only a small quantity remained. This was analysed with the following results:—20·295 cub. cent. gave

Carbonic oxide	11·79
Bisulphide of carbon	4·66
Nitrogen	3·83
	20·28

The analysis was however only approximate, as some sulphuric acid was formed in the combustion of the gas.

A like experiment made with wood-charcoal gave precisely similar results.

Both these experiments proved that the gas at first obtained was due to the organic matter and moisture acting on the bisulphide of carbon and that the latter distilled over unchanged, as soon as the former were removed.

It is unnecessary to describe the other experiments made in the hope of procuring protosulphide of carbon, as they all gave negative results.

Baudrimont gives as evidence of the compositon of the gas obtained by him (1) that lime-water decomposed it into sulphide of calcium and its own volume of carbonic oxide. It is clear that this experiment was not a quantitative one, as no allowance is made for the solubility of the protosulphide of carbon, which is stated to dissolve in its own bulk of water. Hence the result may have been due to a mere mixture of carbonic oxide containing the vapour of bisulphide of carbon and a little sulphuretted hydrogen. (2) Baudrimont states that eudiometric analysis gave equal volumes of CO_2 and SO_2; but this result would be equally attained by the combustion of a gas containing equal volumes of CS_2 and CO; and, at the ordinary temperature, with the diminished pressure in the eudiometer, the tension of CS_2 is more than sufficient to double the volume of gas in the tube. It may further be remarked that Baudrimont does not give any process for removing bisulphide of carbon from the gases obtained by him.

In conclusion, it must be admitted that there is no sufficient evidence of the existence of protosulphide of carbon, all the processes described for its preparation having failed to yield it. Buff and Hofmann* seem to have been equally unsuccessful in their endeavours to obtain it from bisulphide of carbon by electric incandescence.

XXII.—*Notice of a New Ammonio-Chrome Compound.*

BY J. MORLAND, F.C.S.

WHEN sulphocyanide of ammonium is fused, and powdered bichromate of potash added to it, this salt dissolves quietly at first, giving a purple coloration. After a short time, however, a very brisk reaction ensues, ammonia and aqueous vapour are given off abundantly, and the residue is of a beautiful crimson colour. This residue consists of sulphocyanide of ammonium, sulphocyanide of potassium, bichromate of potash, sulphate of potash and the sulphocyanide of a new ammonio-chrome compound; this last salt is easily purified from the others by washing with cold water, in which it is but sparingly soluble, and afterwards by crystallization from alcohol, which dissolves it freely, or from ether, in which it is moderately soluble. This new salt has the composition, $Cr_2\ Csy_3\ 2NH_4O$. Analysis gave the following figures:—

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* Journal of Chemical Society, xii, 283.

	Theory.	Found.	
Cr	18·71	18·71	when the salt was dried at 120° C
S	34·53	34·37	
N	25·18	24·96	
C	12·95	13·27	
H	2·88	3·39	
O	5·76		

This is a perfectly neutral salt, crystallizing in the cubical system. I obtained crystals by the spontaneous evaporation of an ethereal solution, the form of which was the rhombic dodecahedron modified by the planes of the octahedron: it has a strongly bitter taste, especially at the back of the mouth. Heated in a closed tube, it gives off ammoniacal vapours, sulphuretted hydrogen, and some compound of cyanogen with a garlicky odour; the residue is sulphide of chromium, which, when heated in the air, ignites, gives off sulphurous acid, and leaves sesquioxide of chromium.

Neither acids nor alkalies decompose this salt in the cold, but alkalies on boiling throw down oxide of chrome; and acids, when concentrated, decompose it by uniting with the ammonia. Heated on the water-bath with sulphuric acid, it yields sulphate of ammonia and blue sulphate of chrome; oxalic acid gave violet oxalate of chrome and oxalate of ammonia.

Persalts of iron are not coloured by this salt, but nitrate of silver immediately gives a precipitate of uncertain composition, as much of this chrome salt is carried down.

Other chromates as well as bichromate of potash also form this same salt with fused sulphocyanide of ammonium; chromate of potash, and chromate of lead succeed pretty well, but there are also other substances formed. I found the best proportion to be 5 of sulphocyanide to 2 of bichromate, corresponding to 1 eq. bichromate to 5 of sulphocyanide.

Frémy's roseo-chrome salts have the composition

$$(Cr_2O_3.4NH_3).3A,$$

which differs chiefly in the double quantity of ammonia. The cobalt-bases have, according to Frémy, the following compositions :—

$$\begin{array}{ccc} Co_2O_3 & 4 & NH_3 \\ ,, & 5 & ,, \\ ,, & 6 & ,, \end{array}$$

I have attempted to form other compounds by the reduction of chromates in the presence of ammonia-salts, but at present without success.

XXIII.—*On Circular Polarization.*

A Discourse delivered to the Members of the Chemical Society of London.

By Dr. J. H. Gladstone, F.R.S.

When, at the request of the Council, I undertook to bring the subject of circular polarization before the Chemical Society, I did not realize the quantity of the observations which have been recently accumulated by the industry of foreign *savans*. In preparing this discourse, I have been well-nigh overwhelmed with materials, and I have therefore considered it best to omit all description of the more purely physical questions, and to confine myself as closely as possible to those branches of the subject which have a direct bearing on chemical science.

Circular polarization was first observed in quartz by Arago, in 1811; it was investigated by Biot,* and the subject speedily attracted the attention of some of the leading physicists of this country. Brewster, Herschel, and Airy made important discoveries in respect to it; but since that early period, very little has been done by the scientific men of Great Britain, while in France and other parts of the continent, investigations have rapidly extended, and circular polarization has been taken advantage of for the solution of many chemical problems. It is true, that soon after the formation of our Society, Leeson read an elaborate communication on the subject;* some of Pasteur's papers have been translated in our Quarterly Journal,† and the matter has of course been referred to in lectures and treaties on Natural Philosophy;‡ yet there can be no doubt that British Chemists have generally made themselves but little acquainted with the subject.

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* Mem. Inst. 1812, and subsequently.

The leading phenomena of circular polarization are simply these. If a slice be cut from a crystal, endowed with this property, in a direction perpendicular to its axis, and it be examined by polarized light, it does not exhibit the coloured rings and black cross; and if the emergent polarized ray be analysed by a doubly-refracting prism, the two images have complementary colours, which change as the prism is made to revolve. If such a slice of crystal, or a liquid possessing the same power, be placed between the polarizer and analyser of a polariscope, the maximum and minimum of light are in fact not attained when the plane of reflection is inclined to that of polarization at 0° and 90°, but at some other angles 90° apart. The amount of this deflection will differ with the colour—that is, with the refrangibility of the ray; thus a violet ray will be deflected to perhaps twice the distance of a red ray; and hence when white light is employed, a series of colours are observed following one another in regular succession, as the analyser is made to revolve. If, in order to make these follow in their natural order—red, orange, yellow, green, blue, violet—it is necessary to turn the analyser to the right—that is to say, in the direction of the hands of a watch—the substance is said to exhibit right-handed or positive circular polarization, which is usually indicated by the sign ↻ or + : if, on the contrary, the analyser must be turned to the left to produce the same result, the polarization is left-handed, or negative, and the sign ↺ or — is employed. On revolving the analyser beyond the violet rays, the same order of colours, beginning with red, reappears, and there is a transition tint, called by the French *teint de passage* or *teint sensible*, which from its sensitiveness is very valuable for observations.

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* Mem. and Proc. Chem. Soc., ii, 26.

† Chem. Soc. Qu. J., iii, 79; v, 62; vi, 273, 277.

‡ For instance, in Golding Bird's Elements of Natural Philosophy; in Pereira's Lectures, Pharm. J., ii and iii; in Graham's Elements of Chemistry, 2nd Edit., Vol. ii, p. 464; and in a lecture by Maskelyne, Phil. Mag. (4), i, 428.

For the explanation of these phenomena on the undulating theory, I can only refer to Fresnel's Memoirs.*

Substances which exhibit Circular Polarization.—The following table contains a list of the substances in which the phenomena of circular polarization have been observed. It is doubtless incomplete; and it must be borne in mind also that the effects are produced by very many compounds of some of these bodies, which are not included in the table. Against the name of the substance is placed the sign + or −, to indicate the direction of the rotation, and in another column the name of the observer who first remarked the property in the substance in question, or who has worked upon it to the greatest effect. Where a second observer has discovered the existence of a power of rotation in a direction opposite to that first discovered, which is by no means an uncommon circumstance, or has otherwise largely extended our knowledge of the subject, his name has generally been added. The last column indicates whether the substance has been observed to form hemihedral crystals, either itself or in its compounds.

Substance.	Direction.	Authority.	Hemihedral?
Quartz crystal	+ or −	Arago, Biot, Brewster, Herschel	Hem.
Chlorate of soda (solid)..	+ or −	Marbach	Hem.
Bromate of soda (solid)..	+ or −	"	
Acetate of uranium and soda (solid) ..	+ or −	"	
Cinnabar..	+ or −	Descloizeaux	
Oil of turpentine ..	+ or −	Biot, Seebeck, Leeson	
Oil of lemon	+	"	
Oil of bergamotte ..	+	"	
Oil of anise	−	"	
Oil of carraway	+	"	
Oil of spearmint ..	−	"	
Oil of rue	−	"	
Oil of nutmeg	+	Leeson	
Oil of lavender	−	"	
Oil of cubebs	−	Wilhelmy	
Oil of valerian	−	"	
Oil of amber	−	"	
Castor oil	+	"	
Croton oil	+	"	
Balsam of copaiba ..	−	"	
Camphor..	+ or −	Biot, Chantard	

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* Ann. Ch. Phys. (2), xxviii, 147. This is abstracted in Daguin's *Traité Elémentaire de Physique,* which contains many of the most recent observations on the subject.

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THE CHEMICAL SOCIETY.

XXV.—*Contributions to the History of the Phosphorus-Bases.*

By Augustus William Hofmann, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

FIRST MEMOIR.

In a paper* published a few years ago by M. Cahours and myself, the remarkable phosphorus-compounds, whose existence was first pointed out by the experiments of M. Paul Thénard, were subjected to a more complete examination than they had previously received.

The discovery of a better mode of preparation enabled us to gain a clearer view of the nature of this group of substances, and to throw additional light on their relations to the nitrogen-bases; but, owing to the overwhelming number of reactions which presented themselves, we were unable to submit the behaviour of the phosphorus-bases with other groups of bodies to a detailed examination.

In continuation of former experiments, I have lately been much engaged in the investigation of the polyatomic ammonias, the study of which was naturally suggested by the beautiful researches which have been published on the polyatomic alcohols. In the course of these experiments, I frequently had occasion to return to the phosphorus-bases, the employment of triethylphosphine in particular having in many instances led to results which would not easily have been obtained in any other way. The possibility of preparing this body in a state of perfect purity and in considerable quantity, by a series of processes, which, if not quite simple, are at least definite and certain, its position in the system of organic compounds, its conveniently situated boiling-point, the energy and precision of its reactions, and lastly, the simplicity which characterizes these reactions, in consequence of the absence of unreplaced hydrogen in triethylphosphine,—whereby the formation of a large number of compounds of subordinate theoretical interest is excluded,—all these conditions tend strongly to invite us to the study of a body, in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness.

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* Philosophical Transactions, vol. cxlvii, p. 575. Chem. Soc. Qu. vol. xi, p. 56.

It was originally my intention to put together—in one frame, as it were—the various facts which I have collected relating to the phosphorus-bases; but the material lies scattered in so many directions, that I deem it more advisable to publish these observations in a number of shorter memoirs, which, from the nature of the subject, must be more or less fragmentary.

Preparation of Triethylphosphine.—The whole of the material used in my experiments was prepared by the process formerly described in detail by Cahours and myself. The only alteration, which has been found advisable, relates to the separation of the triethylphosphine from the chloride-of-zinc-compound, which is produced by the action of trichloride of phosphorus on zinc-ethyl. It was formerly our practice to throw solid hydrate of potassium into the viscid mass of this salt, and then to dissolve the potassa by gradually dropping water into the retort, the heat resulting from the reaction being sufficient to carry over the base nearly anhydrous. It is better, however, to mix the double salt at once with water, and then decompose it in a retort filled with hydrogen, by allowing strong potassa-solution slowly to flow into it. On subsequently distilling the mixture on a sand bath in a continuous but very slow stream of hydrogen, the triethylphosphine passes over with the aqueous vapour and floats on the top of the condensed water in the receiver. By adopting this mode of proceeding, the reaction is more under the command of the operator, and as the phosphorus-base is not sensibly soluble in water, the quantity of the product is not thereby diminished.

By exact adherence to the prescribed conditions, it is by no means difficult to prepare considerable quantities of pure triethylphosphine; nevertheless the amount obtained is always less than it should be in proportion to the weight of the materials used. This loss is mainly due to the formation of secondary products, which cannot be wholly avoided even when the zinc-ethyl has been carefully prepared, and to partial decomposition of the latter substance during distillation: for it is scarcely possible to imagine a more elegant reaction than that which takes place between trichloride of phosphorus and ready-formed zinc-ethyl. Under these circumstances, many attempts were naturally made to obtain the phosphorus-base in other ways; I have always, however, returned to our original process.

Totally unsuccessful was the attempt to obtain triethylphosphine, without previous preparation of zinc-ethyl, by exposing a mixture of 1 equiv. of trichloride of phosphorus and 3 equivs. of iodide of ethyl with excess of zinc in sealed tubes to a temperature of 150° C. The bodies react under these circumstances; but as only traces of triethylphosphine are produced, I have not thought it worth while to pursue this reaction further. A more favourable result was obtained by heating a mixture of zinc and phosphorus with anhydrous iodide of ethyl to between 150° and 160°. After several hours' digestion, the tubes were found to be coated with white crystals, and a considerable portion of the phosphorus had passed into the red modification. Powerful escape of gas always took place on opening the tubes, and in several instances they were shattered, even when their points were softened in the lamp-flame to diminish the violence of the concussion. Besides zinc-ethyl, the presence of which is indicated by the abundant evolution of hydride of ethyl which is observed on treating the contents of the tube with water, the chief products of this reaction are three phosphorus-compounds, which are formed in proportions varying according to the temperature and the duration of the action.

On extracting the brown residue in the tubes with warm water, and evaporating the clear solution, an oily substance separates which covers the bottom of the dish, and on cooling solidifies into a mass of hard crystals. By repeatedly crystallizing this substance from boiling water and from alcohol, large crystals are obtained, which give off triethylphosphine when treated with potassa even in the cold; by analysis* they were found to consist of a compound of iodide of zinc with iodide of triethylphosphonium, composed according to the formula

$$C_6H_{16}P\,Zn\,I_2 = [(C_2H_5)_3HP]I, Zn\,I.†$$

A solution of iodide of triethylphosphonium mixed with iodide of zinc immediately gives a crystalline compound of exactly similar characters.

The mother-liquor of the double salt yields, when further evaporated, another crystalline body which is more difficult to purify. After three or four crystallizations, however, well-developed crystals are obtained, which do not yield triethylphosphine when treated with potash, either in the cold or with aid of heat.

Analysis shows that this crystalline substance is a compound of iodide of zinc and oxide of triethylphosphine,

$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

The third compound, which remains in the mother-liquor after the two former have crystallized out, and separates, on further evaporation, in beautiful needle-shaped crystals, may be recognized without difficulty as iodide of tetrethylphosphonium. The crystals are insoluble in cold potassa-solution, and give off triethylphosphine only when heated with solid hydrate of potassium.

This iodide likewise unites with iodide of zinc; and as this latter salt is always present in the mother-liquor in considerable quantity, the double salt is generally obtained together with the simple iodide.

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* The combustion of the phosphorus-compounds is not very easily effected. The experiment succeeds best with a mixture of chromate of lead and oxide of copper. All the carbon-determinations quoted in the following pages have been made with this mixture, unless another mode of proceeding is specially stated. All the substances analysed were dried at 100°, except in a few cases, when the mode of drying is also specially mentioned.

The details of the analytical determinations are given in the original papers published in the Philosophical Transactions for 1860.

† $H=1$; $O=16$; $S=32$; $C=12$.

The mode of formation of these compounds is represented by the following equations:—

$$4C_2H_5I + P + 3Zn = [(C_2H_5)_3HP]I, Zn\,I + 2Zn\,I + C_2H_4.$$
$$4C_2H_5I + P + 3Zn = [(C_2H_5)_4P]I, ZnI + 2ZnI.$$

The compound containing oxide of triethylphosphine is evidently formed at the expense of the air in the tube:—

$$(C_2H_5)_3P + O + Zn\,I = (C_2H_5)_3PO, Zn\,I.$$

The above zinc-iodide-compounds of triethyl- and tetrethyl-phosphonium possess interest only in so far as they may serve for the preparation of phosphorus-base. The mixture evaporated to dryness and distilled with hydrate of potassium in an atmosphere of hydrogen, does indeed yield appreciable quantities of triethylphosphine: the action of iodide of ethyl upon a mixture of zinc and phosphorus may therefore be recommended when it is desired to prepare a sample of this remarkable compound without specially arranged apparatus: but it is not adapted for the preparation of the phosphorus-base on the large scale.

I have endeavoured to prepare by this process *triamylphosphine* and *triallylphosphine*, but the results were not such as to encourage me to continue the experiments.

Cahours has recently made similar experiments, but with a difference in the mode of conducting them, which cannot fail to influence the result. Instead of subjecting iodide of ethyl to the action of a mechanical mixture of zinc and phosphorus, he has caused the compound $Zn_3\,P$ to act upon iodide of ethyl at a high temperature. The reaction will doubtless proceed more regularly under these conditions; but the advantage which may perhaps be gained by avoiding the preparation of the zinc-ethyl is compromised, at least in part, by the time and trouble expended in the somewhat complicated preparation of trizinco-phosphide.

Oxide of Triethylphosphine.—The formation of the compound of this oxide with iodide of zinc to which I have alluded, induced me to subject to a careful examination the beautifully crystallized body produced from the phosphorus-base by exposure to the air.

In our former experiments, Cahours and myself had often observed this substance, but we did not succeed in obtaining it in a state of purity fit for analysis. Nevertheless, founding our conclusion on the composition of the corresponding sulphur-compound, and having regard to the analogies presented by the bodies of the arsenic- and antimony-series, we regarded this body as the oxide of the phosphorus-base:

$$C_6H_{15}PO = (C_2H_5)_3PO.$$

I have since confirmed this formula by analysis.

The difficulties which in our former experiments opposed the preparation of this compound in the pure state, arose entirely from the comparatively small quantity of material with which we had to work. Nothing is easier than to obtain this oxide in a state of purity, provided the available quantity of material is sufficient for distillation. In the course of a number of preparations of triethylphosphine for the new experiments, a considerable quantity of the oxide had accumulated in the residues left after distilling the zinc-chloride-compound with potassa. On subjecting these residues to distillation in a copper retort, a considerable quantity of the oxide passed over with the aqueous vapours; and a further quantity was obtained as a tolerably anhydrous but strongly coloured liquid by dry distillation of the solid cake of salts which remained after all the water had passed over. The watery distillate, with or without addition of hydrochloric acid, was evaporated on the water-bath as far as practicable, and the concentrated solution was mixed with solid hydrate of potassium, which immediately separated the oxide in the form of an oily layer floating on the surface of the potash.

The united products were then left in contact with solid potash for twenty-four hours, and again distilled. The first portion of the distillate still contained traces of water, a thin layer of triethylphosphine floating upon the surface. As soon as the distillate solidified, the receiver was changed, and the remaining portion (about nine-tenths) collected apart as the pure product.

With reference to the properties of oxide of triethylphosphine, I may add the following statements to the description formerly given*. This substance crystallizes in beautiful delicate needles, which, if an appreciable quantity of the fused compound be allowed to cool slowly, frequently attain the length of several inches. I have been unable to obtain well-formed crystals; as yet I have not found a solvent from which this substance can be crystallized. It is soluble in all proportions, both in water and alcohol, and separates from these solvents on evaporation in the liquid condition, and solidifies only after every trace of water or alcohol is expelled.

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* Philosophical Transactions, 1857, p. 586; Chem. Soc. Qu., vol xi, p. 66.

Addition of ether to the alcoholic solution precipitates this body likewise as a liquid. The melting point of oxide of triethylphosphine is 44°; the point of solidification at the same temperature. It boils at 240° C. (corrected).

As no determination of the vapour-density of any member of the group of compounds to which the oxide of triethylphosphine belongs has yet been made, it appeared to me of some interest to perform this experiment with the oxide in question. As the quantity of material at my disposal was scarcely sufficient for the determination by Dumas' method, and Gay-Lussac's was inapplicable on account of the high boiling-point of the compound, I adopted a modification of the latter, consisting essentially in generating the vapour in the closed arm of a U-shaped tube filled with mercury and immersed in a copper vessel containing heated paraffin, and calculating its volume from the weight of the mercury driven out of the other arm. As I intend to publish a full description of this method, which promises to be very useful in certain cases, I shall here content myself with stating that the results of my experiments prove the vapour-density of oxide of triethylphosphine to be 66·30, referred to hydrogen as unity, or 4·60 referred to atmospheric air. Assuming that the molecule of oxide of triethylphosphine corresponds to 2 vols. of vapour,* the calculated specific gravity of its vapour $= \frac{134}{2} = 67$, when referred to hydrogen, and 4·63 when referred to air. Hence we may conclude that in oxide of triethylphosphine, the elements are condensed in the same manner as in the majority of thoroughly investigated organic compounds.

From the facility with which triethylphosphine is converted into the oxide by exposure to the air, even at ordinary temperatures, and from the very high boiling-point of the resulting compound, in consequence of which its vapour can exert but very slight tension at ordinary temperatures, I am induced to think that the phosphorus-base may be used in many cases for the volumetric estimation of oxygen. When a paper ball soaked in triethylphosphine is passed up into a portion of air confined over mercury, the mercury immediately begins to rise, and continues to do so for about two hours, after which the volume becomes constant, the diminution corresponding very nearly to the proportion of oxygen in the air. To obtain very exact results, however, it would probably be necessary in every case to remove the residual vapour of triethylphosphine by means of a ball saturated with sulphuric acid.

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* $H_2O = 2$ vols. of vapour.

Oxide of triethylphosphine exhibits in general but small tendency to unite with other bodies; nevertheless it forms crystalline compounds with iodide and bromide of zinc. I have examined more particulaly the zinc-iodide-compound already mentioned.

Oxide of Triethylphosphine and Iodide of Zinc.—On mixing the solutions of the two bodies, the compound separates either as a crystalline precipitate or in oily drops, which soon solidify with crystalline structure. It is easily purified by recrystallization from alcohol and contains—

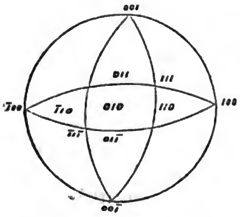
$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

It is remarkable that this compound is formed in presence of a large excess of hydriodic and even of hydrochloric acid.

The crystals melt at 99°: they readily dissolve in warm water, and even more easily in alcohol. From the alcoholic solution well-formed crystals are frequently obtained.

My friend Quintino Sella has examined these crystals.*

Fig. 1.



"System monoclinic:—

100, 101 = 34° 25′; 101, 001 = 48° 48′;

111, 010 = 50° 16′.

Forms observed:—

100, 010, 001, 110, 011, 111, (Fig. 1).

Combinations observed:—

110, 001 (Fig 2).
110, 001; 100 (Figs. 3 & 4).
110, 001; 100, 010 (Fig. 5).
001, 100, 110, 111.
001, 100, 110, 111; 011.
001, 100, 110, 111; 011, 010 (Fig. 6).

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* The details of the crystallographical determinations are given in the original papers published in the Philosophical Transactions for 1860.

Fig. 2.

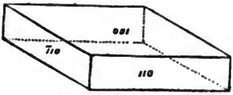


Fig. 3.

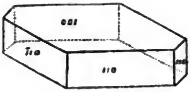


Fig. 4.

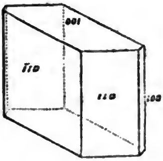


Fig. 5.

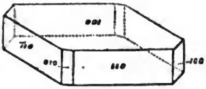
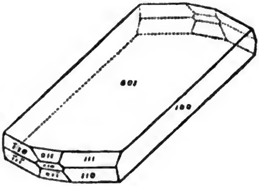
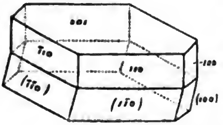


Fig. 6.



Hemitropic crystals with the axis of hemitropy [100], with the face of hemitropy 001.

Fig. 7.



The hemitropic crystals are sometimes simple, as in Fig. 7; sometimes complicated, as in Fig. 8. It is then difficult to distinguish them from trimetric crystals; they become, however, intelligible by assuming that they result from four hemitropic crystals grouped round [100], as in Fig. 9. It is found sometimes that several crystals, like those of Fig. 8, are associated by 001.

Fig. 8.

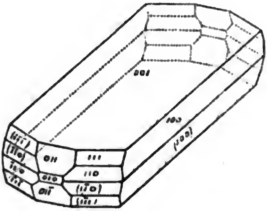
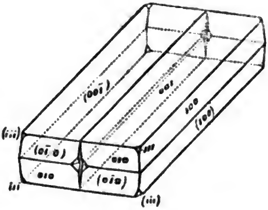


Fig. 9.



It deserves to be noticed that the crystals (Figs. 2, 3, 4, 5, and 7) were formed in the presence of hydrochloric acid, and that in the absence of this acid, only crystals of Fig. 8 are obtained, which, without the study of the cleavage and the optical characters, could not be distinguished from trimetric crystals.

Cleavages 001 and 110 neat and easy. The cleavage 110 of the hemitropic crystals (Fig. 8) exhibits re-entering angles.

Lustre vitreous on the fracture, fatty on the faces.

Hardness somewhat greater than that of gypsum.

The crystals are optically positive; the line of symmetry [010] is their principal medium line. The internal angle of the optical axes differs but little from 78°: and the plane which contains them is nearly perpendicular to the edge of the prism 110.

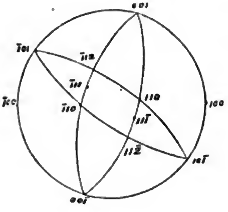
The smallest index of refraction is approximately $\gamma = 1{\cdot}58$."

Oxide of Triethylphosphine and Dichloride of Platinum.—No precipitate is formed on mixing the aqueous solutions of the two compounds, however concentrated; but on adding the anhydrous oxide to a concentrated solution of dichloride of platinum in absolute alcohol, a crystalline platinum-compound is deposited after a few moments. This compound is exceedingly soluble in water, easily soluble in alcohol, insoluble in ether. On adding ether to the alcoholic solution, the salt is precipitated, although with difficulty, in the crystalline state. The alcoholic solution, when evaporating spontaneously, yields beautiful hexagonal plates, frequently of rather large dimensions. On account of its extreme solubility, it is not quite easy to obtain this salt in considerable quantity.

Analysis has led to the somewhat complicated formula

$$C_{24}H_{60}P_4O_3Pt_2Cl_6 = 3[(C_2H_5)_3PO], (C_2H_5)_3PCl_2, 2PtCl_2.$$

Fig. 10.



The platinum-salt has likewise been examined by Quintino Sella.

"System monoclinic:—
100, 101 = 27° 19′; 101, 001 = 46° 23′; 010, 111 = 41° 4′.

Forms observed:—
100, 001, 110, 101, 111, 112 (Fig. 10.)

Combinations observed:—

001, 100, 110. (Fig. 11).
001, 110, $\bar{1}12$, $\bar{1}01$.
001, 110, $\bar{1}12$, $\bar{1}01$, 100, $\bar{1}11$ (Fig. 12).

Fig. 11.

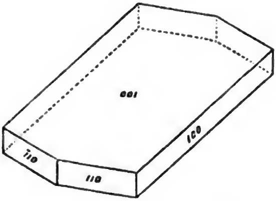
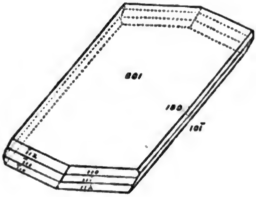


Fig. 12.



Cleavages $\bar{1}01$ and 110 neat and easy.

Colour orange-red.

The optical axes are situated in 010, *i. e.* in the plane of symmetry. They are seen across the faces 001 and the cleavages $\bar{1}01$, and they make an apparent angle of about 64°."

On mixing a concentrated solution of the oxide of triethylphosphine with *trichloride of gold*, a deep-yellow oil is separated, which crystallizes with difficulty after considerable standing. This compound is exceedingly soluble in water and in alcohol. When the aqueous solution is heated, the gold is reduced; the transformation which the oxide of triethylphosphine undergoes in this reaction has not been examined.

Chloride of Tin forms likewise an oily compound with the oxide: I have not succeeded in crystallizing this compound.

Chloride of Mercury is without any action on oxide of triethylphosphine.

Oxychloride of Triethylphosphine.—On passing a current of dry hydrochloric acid through a layer of oxide of triethylphosphine which is fused in a U-shaped tube surrounded by boiling water, brilliant crystals are soon formed. These crystals, however, rapidly disappear, the compound formed in the commencement of the reaction uniting with an excess of hydrochloric acid. The viscous liquid which ultimately remains behind, loses, when heated, the excess of hydrochloric acid, leaving an exceedingly deliquescent crystalline mass, very soluble in alcohol, insoluble in ether.

For analysis, the new compound was washed with absolute ether, and dried over sulphuric acid *in vacuo*, either at the common temperature or at 40°. Three chlorine-determinations in specimens of different preparations led to the formula

$$C_{12}H_{30}P_2OCl_2 = (C_2H_5)_3PO + (C_2H_5)_3PCl_2,$$

which represents an oxychloride of triethyphosphine. The dichloride of triethylphosphine cannot be formed by the action of hydrochloric acid upon the oxide.

The oxychloride exhibits with other compounds the deportment of the oxide. It furnishes with dichloride of platinum the same platinum-salt which is obtained with the oxide. In a similar manner it gives with iodide of zinc the iodide-of-zinc-compound of the oxide previously described. Only once—under conditions not sharply enough observed at the time, and which I was afterwards unable to reproduce in repeated experiments—a compound of the oxychloride with iodide of zinc was formed. This substance, readily soluble in water and alcohol, crystallized from the latter solvent in beautiful colourless transparent octahedra, which, on analysis, gave results, leading to the formula,

$$C_{12}H_{30}P_2OCl_2Zn_2I_2 = (C_2H_5)_3PO,ZnI + (C_2H_5)_3PCl_2,ZnI.$$

Behaviour of Triethylphosphine with Sulphur-compounds.—The remarkable tendency of the phosphorus-base to unite with sulphur has already been mentioned in the previous memoir: the combination of the two bodies is attended with evolution of heat, the result being a beautifully crystalline substance,

$$C_6H_{15}PS = (C_2H_5)_3PS,$$

corresponding to the oxide of triethylphosphine.

This behaviour has induced me to study the action of several sulphur-compounds on the phosphorus-base. In the cases which I have examined, the ultimate product is almost invariably the sulphide of triethylphosphine, already mentioned as resulting from the direct combination of the phosphorus-base with sulphur; but the conditions under which this sulphide is produced vary considerably; and in the majority of cases, it occurs only as a secondary product of the decomposition of other more direct compounds, some of which appeared to me sufficiently interesting to deserve more minute investigation.

In the course of the experiments which I am going to describe, I have prepared considerable quantities of the sulphide of triethylphosphine. This compound, although remarkable for the facility with which it crystallizes, is not easily procured in well-formed crystals. It was only once or twice that I obtained crystals with good faces. They were examined by Quintino Sella, who communicates to me the following results:—

" System rhombohedric:—

$$100, 111 = 54° 35'.$$

Forms observed:—

$$10\bar{1},\ 2\bar{1}\bar{1},\ 210 \text{ (Fig. 13).}$$

Combinations observed:—

$$10\bar{1},\ 210 \text{ (Fig. 14).}$$

$$10\bar{1},\ 210;\ 2\bar{1}\bar{1}.$$

Fig. 13.

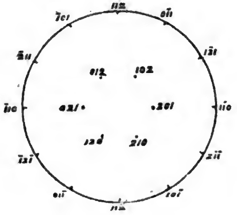
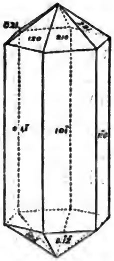


Fig. 14.



At summer heat, the crystals are very soft and flexible; they may be bent 180° without breaking. At lower temperatures, they are harder and much less flexible.

The crystals are optically positive. The index of refraction for the extraordinary ray $\epsilon = 1{\cdot}65$, and for the ordinary ray $\omega = 1{\cdot}59$.

Behaviour of Triethylphosphine with Sulphuretted Hydrogen.— The phosphorus-base has no action on *sulphuretted hydrogen*.

When it is brought in contact with hydrosulphuric acid over mercury, the gas does not exhibit any alteration. No sulphide of triethylphosphine is formed, even in presence of air, as might indeed have been expected. The attraction of the phosphorus-base for oxygen prevents the oxidation of the sulphuretted hydrogen; a solution of this gas in water, when mixed with a few drops of triethylphosphine, may be preserved in air-filled vessels much longer than without this addition.

Behaviour of Triethylphosphine with Sulphide of Nitrogen.—*Sulphide of Nitrogen*, NS, prepared as recommended by Fordos and Gelis, viz., by the action of ammonia on chloride of sulphur dissolved in disulphide of carbon, is decomposed by triethylphosphine, with evolution of light and heat. Gas is evolved, and at the same time a yellowish liquid is produced, which, on cooling, solidifies into a fibrous mass of crystals of the sulphide.

Behaviour of Triethylphosphine with Mercaptan.—When these two bodies are mixed together in an atmosphere of carbonic acid, no alteration takes place, even if they are left in contact for some time, or if they are heated to 100° in sealed tubes for twenty-four hours. But if the mixture be poured into an air-filled flask, crystals of sulphide of triethylphosphine make their appearance in a few hours. The crystals increase if the air has free access to the mixture; but if the flask be corked, the crystallization is interrupted. On opening the flask, the entry of the air may be recognized by the light cloud which the phosphorus-base, diffused through the atmosphere of the vessel, forms with the oxygen. When a mixture containing excess of mercaptan was left for a few days in an open flask, every trace of phosphorus-base had disappeared, and the remaining colourless liquid was filled with crystals of the sulphide. On mixing this liquid with water, it separated into two layers, the upper of which quickly solidified, especially on exposure to the air, to an imperfectly crystalline mass, easily recognized as a mixture of sulphide of triethylphosphine with excess of mercaptan. The impure crystals were exposed for a while to the air and then recrystallized from boiling water, when, on analysis, they gave results agreeing with the formula

$$C_6H_{15}PS = (C_2H_5)_3PS.$$

The lower stratum of liquid is aqueous alcohol containing small quantities of oxide of triethylphosphine and mercaptan. To remove the latter, the liquid was shaken up with recently precipitated mercuric oxide and distilled. The distillate, rectified several times over lime, yielded a clear liquid, which burnt with a colourless flame and exhibited all the characters of alcohol.

The interpretation of this result appears at the first glance exceedingly simple; the sulphide of triethylphosphine cannot be formed directly from the phosphorus-base, but owes its origin to the oxide first produced by the action of air, this oxide being decomposed by the mercaptan and yielding sulphide of triethylphosphine and alcohol:

$$(C_2H_5)_3PO + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\} S = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\} O + (C_2H_5)_3PS.$$

Experiment shows, however, that this equation illustrates only the final result of the reaction. Oxide of triethylphosphine and mercaptan, brought together under the most various conditions at ordinary temperatures and under pressure, do not yield a trace of sulphide of triethylphosphine; and we have to suppose, therefore, that the mercaptan interchanges its sulphur with the oxygen of the oxide of triethylphosphine, only at the instant of formation of the latter, or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

In connection with this subject, various attempts were made to replace the oxygen in oxide of triethylphosphine by sulphur. But neither by treatment with sulphide of ammonium, nor by continued boiling with the higher sulphides of potassium, could the oxide be converted into the corresponding sulphide, whereas the conversion of the sulphide into the oxide takes place without any difficulty. This, however, is not more than might have been expected from the behaviour of the oxide with hydrochloric acid, mentioned in one of the preceding paragraphs. The different degrees of stability which characterize the oxide and the sulphide of triethylphosphine may also be strikingly seen in the behaviour of these compounds with sodium, the sulphide being reduced, with the greatest facility, to free triethylphosphine, even below the melting-point of the sodium, whereas the oxide may be distilled from sodium without experiencing the slightest alteration.* Ebullition with ordinary concentrated nitric acid likewise converts the sulphide into the oxide, the sulphur being at the same time transformed into sulphuric acid. The liquid filtered off from the precipitate obtained by barium-salts, when evaporated to dryness and fused with nitrate of potassium, yields no further trace of sulphur.

Behaviour of Triethylphosphine with Disulphide of Carbon.— These two bodies, when mixed in the anhydrous state, act upon one another with considerable force, amounting frequently to explosive violence, and unite into a red crystalline mass. The compound is best prepared by mixing the solutions of its constituents in alcohol or ether: the new body then instantly separates in beautiful red crystalline laminæ.

Several times recrystallized from alcohol and dried over sulphuric acid, the new body has furnished results leading to the formula,

$$C_7\,H_{15}\,PS_2 = (C_2H_5)_3\,P + CS_2.$$

The red crystals are not the only product of the action of disulphide of carbon on triethylphosphine. A second beautifully crystallized compound is deposited after some time from the mother-liquor. This substance is formed in extremely minute quantity: its nature is not yet established.

The compound of triethylphosphine with disulphide of carbon is insoluble in water, sparingly soluble in ether, moderately soluble in disulphide of carbon, and somewhat more soluble in alcohol, especially when heated. The solution has no action on vegetable colours. From the boiling alcoholic solution, it separates on coolin red needles, somewhat resembling the crystals of chromic acid, which are formed by the action of strong sulphuric acid on a solution of chromate of potassium. The ethereal solution, left to evaporate in an open cylinder, deposits finely developed, deep-red crystals of considerable size. Quintino Sella has examined these crystals with the following results.

---

* In the previous memoir, it is stated that the phosphorus-base is reproduced from the oxide by the action of metallic sodium. Probably the oxide used in the former experiments contained a small quantity of free triethylphosphine, and thus led to an erroneous statement.

"System monoclinic :—

100, 101 = 29° 41½′; 010, 111 = 74° 4′; 101, 001 = 27° 7½′.

Forms observed :—

100, 010, 001, 110, $\bar{1}01$ (Fig. 15.)

Combinations observed :—

100, 110, 001, $\bar{1}01$ (Fig. 16.)
100, 110, 001, $\bar{1}01$, 010 (Fig. 17.)

Fig. 15.

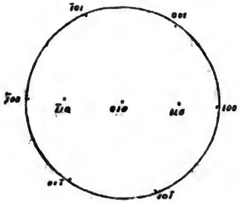


Fig. 16.

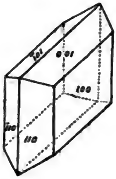
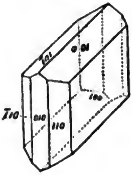


Fig. 17.



Cleavages :—010, 100, neat and easy.

The crystals are optically positive: the medium-line coincides with the axis of symmetry [010]. The interior angle of the optical axes is not very different from 70°. The plane of the optical axes is nearly parallel to the face 001. The axis of symmetry, or of smallest elasticity, exhibits a violet-red colour, which even in very thin layers is very intense. The axis nearly parallel to [100], or the axis of greatest elasticity, exhibits a similar but much lighter red tint. The normal shows in thin layers a straw-yellow, in thicker layers an orange-yellow colour. In polarized light, one of the most beautiful examples of dichroism is observed by looking across the faces 010, the colour passing in the case of thin layers from a pure yellow to a deep red. But even in ordinary light the dichroism is perceptible; for the light passes with a violet-red across the faces 100, and with an orange-red colour of far less intensity across the faces 010.

Hardness less than that of gypsum."

The red crystals appear to possess the character of a weak base. They dissolve in strong hydrochloric acid, forming a colourless liquid, from which potassa or ammonia throws down the compound in its original state, though somewhat lighter in colour, on account of its minute state of division. The acid solution forms with dichloride of platinum a light yellow amorphous salt, insoluble in alcohol and ether, which changes colour and somewhat decomposes on drying. It darkens in colour, even when dried *in vacuo*, hydrochloric acid fumes being evolved. The analysis of a slightly decomposed salt gave results approximately agreeing with the formula,

$$(C_2 H_5)_3 P, CS_2, H Cl, PtCl_2.$$

The gold-salt is obtained like the platinum-salt, and exhibits similar properties.

It is not very easy to form a clear notion of the constitution of the red crystals. According to the formula, the compound is the primary triethylphosphonium-salt of sulphocarbonic acid *minus* 1 equiv. of sulphuretted hydrogen, and corresponds therefore to sulphocarbamic acid, the ammonium salt of which, as is well known, is produced by the action of ammonia on disulphide of carbon. There is, however, no analogy in the constitution of the two substances.

The red crystals exhibit a remarkable tendency to pass into the sulphide of triethylphosphine. On mixing their alcoholic solution with oxide or nitrate of silver, carbonic acid is evolved, sulphide of silver and metallic silver are separated, and the filtered solution, when evaporated, deposits crystals of the sulphide:

$$(C_2 H_5)_3 P, CS_2 + 2Ag_2 O = Ag_2 S + Ag_2 + CO_2 + (C_2H_5)_3 PS.$$

The disulphide-of-carbon-compound undergoes a similar change, even under the influence of moisture. Crystals which had not been dried with sufficient care, were changed, after a few months, when kept in corked tubes, into a yellowish white, semifluid mass, of peculiar odour, which, by recrystallization from boiling water, furnished a considerable quantity of pure sulphide of triethylphosphine. To establish this transformation by numbers, the purified crystals were identified by analysis.

It is obvious that the transformation of the red crystals into the sulphide involves the co-operation of the elements of water. Perfectly dry crystals were preserved in sealed tubes for many months without the slightest alteration. The crystals fuse at 95° and volatilize at 100°; in the absence of moisture, they may be heated, under pressure to 150° without undergoing any decomposition. The phenomena are very different in the presence of water. When exposed for some days in sealed tubes with water to a temperature of 100°, the red crystals are gradually transformed into white needles, which are easily recognized as sulphide of triethylphosphine. The transformation is independent of atmospheric air: for it takes place with equal facility in vessels with air, or carbonic acid, or *in vacuo*.

The products which accompany the sulphide formed in this reaction vary according to the time during which the red crystals are digested with water. If the tubes be allowed to cool after one or two days' digestion, the liquid generally becomes filled with white needles, which are, however, still intermixed with red prisms, showing that the transformation is not yet complete. Scarcely any gas escapes when the tubes are opened, but when gently heated, the liquid yields abundance of disulphide of carbon. On the other hand, when the tubes are heated until the transformation of the red compound is accomplished,—which generally takes place after three or four days' digestion,—a large volume of gas escapes on opening the tubes, and they are occasionally shattered. The gas which is thus evolved consists of sulphuretted hydrogen and carbonic acid, which are obviously secondary products of the reaction, arising from the protracted action of the water upon the disulphide of carbon, which is separated in the first stage of the process. The liquid from which the crystals of sulphide have been deposited has a distinctly alkaline reaction, which belongs neither to the sulphide nor to the red crystals from which the sulphide arises, both these compounds being without action on vegetable colours. To seize the basic substance, the liquid was evaporated on the water-bath, till the sulphide had been as far as possible expelled, and then precipitated with iodide of zinc, which does not combine with the sulphide, traces of this body which might have remained, being in this manner eliminated. The iodide-of-zinc-precipitate was semisolid, and slowly became crystalline on treatment with alcohol; it did not, however, exhibit a sufficiently definite appearance to warrant its analysis. The bases were therefore at once liberated again by digesting the precipitate with oxide of silver; the powerfully alkaline liquid thus obtained gave, on addition of hydrochloric acid and dichloride of platinum, a difficultly soluble platinum-salt, crystallizing, after the necessary purification, from boiling water, in splendid octohedra, which on analysis proved to be the methyl-triethylphosphonium-compound.

The solution filtered off from the octohedral salt gave, on evaporation, the extremely soluble six-sided tables of the platinum-salt of oxide of triethylphosphine, which I have mentioned in the commencement of this paper.

The products of the action of water upon the red crystals, then, are sulphide of triethylphosphine—the principal product—oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide-of-carbon-compound and two molecules of water contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon:

$$4[(C_2H_5)_3P{\cdot}CS_2] + 2\left[\left.\begin{matrix}H\\H\end{matrix}\right\}O\right] = 2[(C_2H_5)_3PS] + (C_2H_5)_3PO + \left.\begin{matrix}[(CH_3)(C_2H_5)_3P]\\H\end{matrix}\right\}O + 3CS_2.$$

Whilst engaged with the experiments involved in the elucidation of this subject, I observed occasionally small well-defined yellow crystals disseminated among the mixture of white and red needles, which are deposited when the digestion-tubes are allowed to cool, before the transformation is terminated. The yellow crystals appeared in greater quantity towards the close of the operation, and were found to be a secondary product formed by the action of the sulphuretted hydrogen, which is generated in the last stage of the process. I have since learnt to prepare the yellow crystals by a simpler and more definite method. This remarkable compound has become the starting-point of a new enquiry, the result of which I reserve for a later communication.

The formation of the red crystals by the union of triethylphosphine and disulphide of carbon takes place so rapidly, and with such facility, that ever since the first time I observed this phenomenon, I have used the disulphide of carbon as a reagent for the detection of the phosphorus-bases: for trimethylphosphine exhibits a deportment perfectly similar to that of the ethyl-body. The minutest quantities of these bases may thus be readily and safely recognized. The reaction is best observed by pouring the liquid to be examined upon a watch-glass, and allowing the vapour of the disulphide of carbon to flow from an inclined bottle upon the liquid. The watch-glass immediately becomes coated with a beautiful net-work of the red crystals. It requires scarcely to be mentioned that the crystals are formed only when the phosphorus-bases are free. They appear, however, readily on adding to a mixture of their salts and disulphide of carbon, a drop of potash, which liberates the bases.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance, which in delicacy could be compared with it. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas may, as I have shown already in another place,* be recognized without any difficulty.

In order to satisfy myself that disulphide of carbon may be employed with safety as a test for the phosphorus-bases, it was necessary to examine the deportment of this compound with the *arsines* and *stibines*. Disulphide of carbon exhibits no reaction with *triethylarsine* and *triethylstibine*. I have left mixtures of these bases with the disulphide in contact for a considerable length of time, both at the common temperature and at 100°, without being able to observe the slightest alteration. I have also satisfied myself that disulphide cf carbon, at all events in the common temperature, is without action upon *phosphoretted hydrogen*.

In examining somewhat minutely into the deportment of triethylphosphine with sulphur-compounds, the organic sulphocyanates could not be left unnoticed. My attention was in the first place fixed by the sulphocyanate of phenyl, which I had just discovered at the time I was engaged in the study of these reactions.

Action of Sulphocyanate of Phenyl upon Triethylphosphine. The reaction between the two substances in the anhydrous state is very violent, and frequently causes the inflammation of the phosphorus-base. The mixture assumes a deep-yellow colour, and on cooling deposits sometimes splendid uranium-yellow needles; often, however, it remains liquid for hours, and even for days, but suddenly solidifies, when touched with a glass rod, into a hard yellow crystalline mass. The new compound is most conveniently prepared by allowing the sulphocyanate to act upon the triethylphosphine in the presence of a considerable volume of ether. The product of the reaction, being difficultly soluble in cold ether, often separates in the crystalline state, more frequently as an oil, which solidifies after some time. In order to ensure perfect purity, it is only necessary to crystallize the compound once or twice from boiling ether.

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* Quarterly Journal of the Chemical Society, vol. xiii.. p. 87.

The numbers obtained in analysis characterize the new body as a combination of one molecule of triethylphosphine with one molecule of sulphocyanate of phenyl:

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P+\left.\begin{matrix}CN\\C_6H_5\end{matrix}\right\}S=C_{13}H_{20}NPS.$$

The above formula is fully corroborated by the analysis of several well-defined salts, which will be mentioned presently.

The yellow crystals are insoluble in water. Alcohol, both cold and hot, dissolves them in almost every proportion. The best crystals were obtained by the spontaneous evaporation of the ethereal solution in high open cylinders. Some of these crystals were so well developed, that Quintino Sella was enabled to submit them to a detailed crystallographic examination, an abstract of which I here insert.

"System monoclinic:—

100, 001 = 61° 2′; 010, 110=44° 27′.

Forms observed:—

100, 010, 001, 110 (Fig. 18).

Combinations observed:—

110, 001 (Fig. 19).
110, 100, 001 (Fig. 20).
110, 001; 100, 010 (Fig. 21).

Fig. 18.

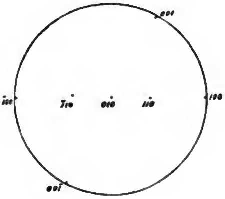


Fig. 19.

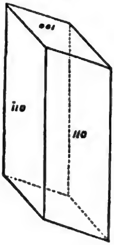


Fig. 20.

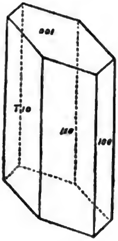
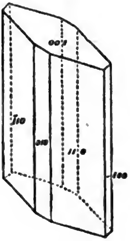


Fig. 21.



Cleavage 100 easy; cleavage 110 fibrous.

Hardness nearly that of gypsum.

If we endeavour to associate this compound with well-known bodies, in order to obtain some insight into the probable arrangement of its proximate constituents, both its formation and its deportment point to *urea*. Urea is generated by the combination of ammonia and cyanic acid; the yellow crystals are formed by the union of two compounds derived respectively from ammonia and cyanic acid. In urea the faculty possessed by ammonia of combining with acids has been preserved; the new compound likewise exhibits the sharply defined characters of a monacid base. Whatever constitution be attributed to urea, must also be claimed for the new base. If urea be viewed as a monacid diamine,

$$CH_4N_2O = \left.\begin{matrix} (CO)'' \\ H_2 \\ H_2 \end{matrix}\right\} N_2,$$

the yellow crystals present themselves as

$$C_{13}H_{20}NPS = \left.\begin{matrix} (CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_6H_5) \end{matrix}\right\} NP.$$

The new compound accordingly belongs to the type urea: it may be viewed as ordinary urea, the oxygen of which is replaced by sulphur, and the hydrogen by ethyl and phenyl, whilst phosphorus has taken the place of half the nitrogen. Regarded from this point of view, the formation of the new compound presents considerable interest: it offers the first example of the perfect substitution of the hydrogen in urea, which had remained doubtful hitherto, and illustrates in a remarkable manner the persistence of the type urea under the influence of an almost overwhelming substitution. At the same time it deserves to be noticed that the corresponding oxygenated urea remains to be discovered.

The new compound, as already mentioned, possesses the properties of a well-defined organic base. Insoluble in water, it dissolves with the greatest facility even in very diluted acids, giving rise in many cases to easily-crystallizable salts which are capable of double decomposition, and from which the base may be reprecipitated by the careful addition of potassa or ammonia.

Chloride.—The solution of the phenyl-compound in warm concentrated hydrochloric acid solidifies on cooling to a crystalline mass, which, when recrystallized from moderately warm water, furnishes splendid cadmium-yellow crystals, frequently an inch in length. Boiling water has to be avoided, since it decomposes the substance. Even the dry crystals are altered at 100°; they must therefore, like all the other salts of the base, be dried *in vacuo* over sulphuric acid.

The chloride is composed according to the formula

$$C_{13}H_{21}NPSCl = \left[\left.\begin{array}{l}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{array}\right\} NP\right] Cl.$$

Bromide.—Both in preparation and properities, precisely similar to the salt previously mentioned. It contains

$$C_{13}H_{21}NPSBr = \left[\left.\begin{array}{l}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{array}\right\} NP\right] Br.$$

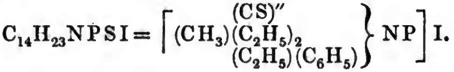
Platinum-salt.—The solution of the chloride furnishes with dichloride of platinum a light-yellow crystalline precipitate. Dilute solutions slowly deposit this salt in somewhat better-formed crystals, which are frequently grouped in lily-shaped aggregations. It was found to contain

$$C_{13}H_{21}NPSPtCl_3 = \left[\left.\begin{array}{l}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{array}\right\} NP\right] Cl, PtCl_2.$$

I did not succeed in preparing the sulphate or the nitrate of the base. The phenyl-compound is rapidly decomposed under the influence of these acids; it forms, however, beautifully crystallized salts with the iodides of methyl and ethyl. I have examined only the former of these compounds.

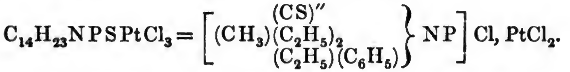
Iodide-of-Methyl-compound.—When iodide of methyl is poured into an ethereal solution of the urea, the new compound is at once separated as a heavy oil which rapidly solidifies into a crystalline mass. The crystals dissolve in boiling water which on cooling deposits the iodide in splendid needles of a golden-yellow colour.

These crystals contain



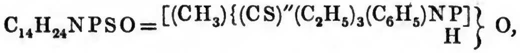
$$C_{14}H_{23}NPSI = \left[\left.\begin{matrix} & (CS)'' \\ (CH_3) & (C_2H_5)_2 \\ & (C_2H_5)(C_6H_5) \end{matrix}\right\} NP\right] I.$$

Platinum-salt of the Methyl-compound.—The chloride obtained by treating the iodide with chloride of silver, yields on addition of dichloride of platinum, an acicular platinum-salt, which may be recrystallized without decomposition from boiling water. Its composition corresponds to that of the iodide:



$$C_{14}H_{23}NPSPtCl_3 = \left[\left.\begin{matrix} & (CS)'' \\ (CH_3) & (C_2H_5)_2 \\ & (C_2H_5)(C_6H_5) \end{matrix}\right\} NP\right] Cl, PtCl_2.$$

The iodide, when treated with oxide of silver, furnishes, together with iodide of silver, a very caustic liquid containing the corresponding oxide. The presence in this liquid of the compound,



$$C_{14}H_{24}NPSO = \left.\begin{matrix} [(CH_3)\{(CS)''(C_2H_5)_3(C_6H_5)NP] \\ H \end{matrix}\right\} O,$$

is proved by the fact of the characteristic needle-shaped platinum-salt being immediately reproduced when it is saturated with hydrochloric acid and mixed with dichloride of platinum. The free base is, however, readily decomposed. On boiling, the odour of sulphocyanate of phenyl becomes at once perceptible; if ebullition be continued until the odour has disappeared, addition of hydrochloric acid and dichloride of platinum no longer furnishes the difficulty soluble needles. In their place, large well-developed orange-yellow octahedra are deposited on evaporation, which by analysis were found to be the platinum-salt of methyl-triethyl-phosphonium.

The free methylated phenyl-base then simply splits, by ebullition, into sulphocyanate of phenyl and oxide of methyl-triethylphosphonium. When the solution is boiled by itself, the sulphocyanate is separated as such; when it is boiled in the presence of oxide of silver, the sulphocyanate is, partly at least, destroyed, the alkaline solution becoming acid and exhibiting the presence of considerable quantities of sulphuric acid. This transformation clearly shows how feebly the proximate constituents are held together in the urea. The same instability is perceptible in the general deportment of the compound. Even extremely dilute nitric acid liberates the sulphocyanate of phenyl, whilst the phosphorus-base is converted into the oxide. The chloride is one of the more stable salts of the urea, but it is likewise readily altered: on addition of a large quantity of water, the solution of the salt becomes milky, the sulphocyanate of phenyl being separated in oily globules, and now contains the chloride of triethylphosphonium. On adding ammonia to the *concentrated* solution of the chloride, the urea, as already stated, is separated without change, and may be easily recovered by taking up with ether and crystallizing. If, on the other hand, the *dilute* solution be boiled with ammonia, the turbidity perceptible in the commencement disappears again, and after a few moments beautiful crystals of *phenyl-sulphocarbamide* are deposited, triethylphosphine being simultaneously liberated:

$$\left.\begin{array}{l}(CS)''\\(C_2H_5)_3\\(C_6H_5)\end{array}\right\}NP+H_3N=(C_2H_5)_3P+\left.\begin{array}{c}(CS)''\\(C_6H_5)\\H_3\end{array}\right\}N_2.$$

On treating the chloride with potassa, phenomena exactly analogous are observed; the crystals which are separated, are, however, *diphenyl-sulphocarbamide:*

$$2\left[\left.\begin{array}{l}(CS)''\\(C_2H_5)_3\\(C_6H_5)\end{array}\right\}NP\right]+4\left[\left.\begin{array}{c}K\\H\end{array}\right\}O\right]=\left.\begin{array}{c}K\\K\end{array}\right\}S+\left.\begin{array}{c}K\\K\end{array}\right\}CO_3+\left.\begin{array}{c}H\\H\end{array}\right\}O$$
$$+\,2[(C_2H_5)_3P]+\left.\begin{array}{c}(CS)''\\(C_6H_5)_2\\H_2\end{array}\right\}N_2.$$

If a few drops of disulphide of carbon be added to the solution of the urea, the liquid, when gently heated, assumes a deep red colour, and deposits on cooling the beautiful ruby-red crystals $(C_2H_5)_3P,CS_2$, which I have mentioned in a previous paragraph of this paper. The mother-liquor of these crystals furnishes on evaporation oily droplets of sulphocyanate of phenyl. The urea, even when perfectly pure and dry, cannot be preserved without undergoing a gradual alteration. If the crystals be left under a bell-jar containing atmospheric air, they become dull, and at last moist and sticky, whilst a peculiar extremely disagreeable odour, distantly resembling that of hydrocyanic acid, becomes perceptible; at the same time, a delicate net-work of fine needles begins to appear on the glass, easily recognized as sulphide of triethylphosphine. The crystals of the urea fuse at 57°·5, forming a yellow liquid, which, in consequence of incipient decomposition, resolidifies but slowly and imperfectly. At 100°, the phenomena just mentioned are much more distinctly observed, and especially the smelling body is unmistakeably perceived. The peculiar smelling body is likewise almost overwhelmingly produced on evaporating the ethereal mother-liquor of the compound. As yet I have not been able to lay hold of the possessor of this remarkable odour. The ethereal mother-liquor, when evaporated, leaves a brown syrup, which after some time deposits large crystals of sulphide of triethylphosphine. Submitted to distillation, this residue yields, together with other products, an additional quantity of the crystallized sulphur-compound.

Transformations precisely similar are observed when the crystals of the urea, in sealed tubes, are exposed to a temperature of from 150° to 160°. The brown fused mass which is thus formed, solidifies on cooling with crystalline structure; the crystals, however, are no longer the original compound, but sulphide of triethylphosphine, which is surrounded by another substance. The examination of this reaction has not yet been completed. The nature of the final product of the metamorphosis may, however, be anticipated, in some measure, by the results obtained in studying the deportment of triethylphosphine with *sulphocyanate of ethyl* and *sulphocyanate of ethylene*, which will be briefly mentioned in some of the following paragraphs.

Action of Sulphocyanate of Allyl upon Triethylphosphine.—To generalize the relations established in the preceding paragraph, I was induced to examine the deportment of the phosphorus-base with oil of mustard. The two bodies act upon each other with extraordinary violence; the mixture turns brown, but does not solidify either by cooling or by agitation. After some days, however, the syrup yields brown crystals which are difficult to purify. The purification of the compound succeeds, however, without any difficulty when the reaction is allowed to take place in ether. In this manner a crystalline mass is easily obtained, which requires only to be washed with cold ether, and then once recrystallized from boiling ether.

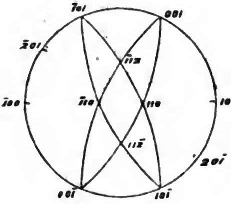
It has the formula,

$$C_{10}H_{20}NPS = \left.\begin{matrix}(CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_3H_5)\end{matrix}\right\} NP.$$

The allyl-compound behaves in all respects like the phenyl-compound. It is insoluble in water, but easily soluble in alcohol; the solution has a faintly alkaline reaction. It fuses at 68° and solidifies at 61°. At a higher temperature, it is decomposed exactly like the phenyl-compound. In this case also, a peculiar, and if possible, still more repulsive odour is evolved, while crystals of sulphide of triethylphosphine separate in large quantity.

The allyl-compound crystallizes with extraordinary facility. There is no difficulty in obtaining it in colourless transparent crystals half an inch in length, and perfectly developed on all sides. I scarcely remember any other organic compound that crystallizes so readily. The crystals, as appears from the measurements of Quintino Sella, are isomorphous with those of the phenyl-compound. Sella has communicated to me the following details respecting his examination.

Fig. 22.



"System monoclinic:—

100, 101 = 35° 42′; 001, 101 = 29° 3′;
010, 111 = 39° 22′.

Forms observed:—

100, 001, 110, 1̄01, 2̄01, 1̄12 (Fig. 22).

Combinations observed:—

001, 100, 110 (Fig. 23).

001, $\bar{1}01$, 110 (Fig. 24).

100, 001, $\bar{1}01$, 110 (Fig. 25).

100, 001, $\bar{1}01$, 110, $\bar{1}12$ (Fig. 26).

100, 001, $\bar{1}01$, 110, $\bar{2}01$, $\bar{1}12$ (Fig. 27).

Fig. 23.

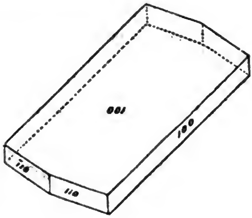


Fig. 24.

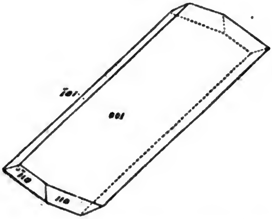
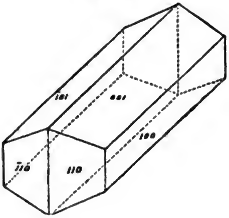


Fig. 25.



The form $\bar{1}12$ is sometimes hemihedral.
Cleavages 100 and 001 neat, easy.

Fig. 26.

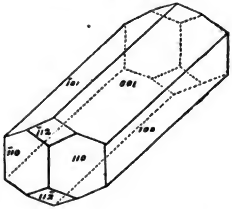
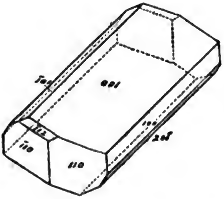


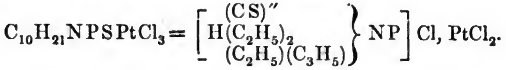
Fig. 27.



The optical axes are situated in the plane of symmetry, viz., 010; their principal medium is perpendicular to $\bar{1}01$, and their internal angle is about 72½°. The index of refraction of the ray vibrating parallel to the axis of symmetry is $\beta = 1{\cdot}657$.

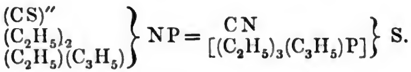
Hardness less than that of gypsum."

Platinum-salt.—I have contented myself with verifying the formula of the allyl-urea by the analysis of the platinum-salt. The allyl-compound dissolves readily in hydrochloric acid, and the solution, when mixed with dichloride of platinum, yields a light-yellow scaly precipitate having a silky lustre, which fuses to a yellow oil in boiling water, and is represented by the formula—



$$C_{10}H_{21}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{matrix}\right\}NP\right]Cl, PtCl_2.$$

The allyl-base described in the preceding pages has the composition of sulphocyanide of triethyl-allylphosphonium.



$$\left.\begin{matrix}(CS)''\\ (C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{matrix}\right\}NP = \left.\begin{matrix}CN\\ [(C_2H_5)_3(C_3H_5)P]\end{matrix}\right\}S.$$

I felt some interest in comparing the latter compound with the allyl-base. Iodide of allyl acts with the greatest energy upon triethylphosphine. The solid product of the reaction, recrystallized from alcohol, furnishes splendid needles of iodide of triethyl-allylphosphonium, which, by analysis, was found to contain—

$$[(C_2H_5)_3(C_3H_5)P]I.$$

Treatment with chloride and oxide of silver yields the corresponding chloride and hydrate. They resemble in every respect the tetrethylphosphonium-compounds. The chloride gives with dichloride of platinum an easily crystallizable octohedral platinum-salt.

The hydrate of triethyl-allylphosphonium forms with hydrosulphocyanic acid a difficultly crystallizable salt which is easily soluble in water, and differs, as might have been expected, entirely from the allyl-base which has the same composition.

Behaviour of Triethylphosphine with the Sulphocyanates of Ethyl and Ethylene.—I have in vain endeavoured to produce, by the action of triethylphosphine on the sulphocyanates of methyl, ethyl, and amyl, compound ureas analogous to the allyl- and phenyl-bodies. It is true that these substances act upon triethylphosphine even at ordinary temperatures; in the case of sulphocyanate of methyl, indeed, the action is very brisk, but I did not succeed in obtaining definite compounds. Sulphocyanate of ethyl remained for months in contact with triethylphosphine without depositing any crystalline compound. The non-production of these ureas cannot, however, excite surprise, if we remember in how many respects, and especially in the relation to ammonia, the sulphocyanogen-compounds of ethyl and its homologues differ from those of allyl and phenyl.

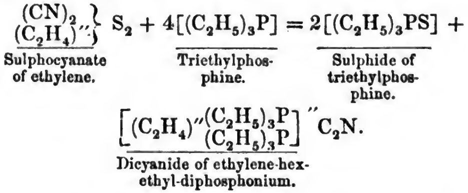
When a mixture of triethylphosphine and one of the abovementioned sulphocyanates is heated for some hours in a sealed tube to 100°, an abundant crop of crystals of sulphide of triethylphosphine is deposited from the liquid. These crystals are surrounded by a brown viscid substance, soluble to a certain extent in water, easily soluble with green colour in alcohol. In order to disentangle from this mixture the complementary product of the reaction, the liquor was shaken with ether to separate the sulphide, evaporated with an excess of hydrochloric acid, and the residue redissolved in water, when a quantity of the brown impurities remained insoluble. The filtered solution gave with trichloride of gold a dingy yellow precipitate, which, by treatment with sulphuretted hydrogen, reprecipitation of the separated chloride by trichloride of gold, &c., ultimately assumed the characters of the pure gold-salt of triethylphosphonium which was identified by analysis. The beautifully orange-yellow platinum-salt was likewise analysed.

The action of sulphocyanate of ethyl upon triethylphosphine may be accordingly represented by the equation:

$$\left.\begin{matrix}C\,N\\C_2H_5\end{matrix}\right\}S + 2[(C_2H_5)_3P] + \left.\begin{matrix}H\\H\end{matrix}\right\}O = (C_2H_5)_3PS + \left.\begin{matrix}[(C_2H_5)_4P]\\H\end{matrix}\right\}O + HCN.$$

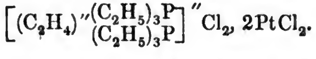
I have not been able to trace directly the hydrocyanic acid which figures in this equation, but this acid appears unmistakeably in its products of decomposition. The brown substance, which accompanies the sulphide of triethylphosphine and the hydrate of tetrethylphosphonium, is rich in nitrogen: boiled for some time with hydrochloric acid, it yields abundance of chloride of ammonium.

I have likewise examined the behaviour of disulphocyanate of ethylene with triethylphosphine. The reaction takes place with energy at ordinary temperatures. When triethylphosphine is poured into a concentrated alcoholic solution of sulphocyanate of ethylene, the liquid immediately solidifies to a dazzling white crystalline mass of sulphide of triethylphosphine. It deserves to be noticed that the same decomposition takes place also when the substances are allowed to react in presence of anhydrous ether. The transformation which the sulphocyanate of ethylene undergoes under the influence of triethylphosphine is perfectly analogous to the change of the ethyl-compound when submitted to the same agent. Instead of a derivative of tetrethylphosphonium, the sulphocyanate of ethylene produces the cyanide of a diatomic metal, of *ethylene-hexethyl-diphosphonium*:



$$\underbrace{\left.\begin{matrix}(CN)_2\\(C_2H_4)''\end{matrix}\right\}}_{\text{Sulphocyanate of ethylene.}} S_2 + 4\underbrace{[(C_2H_5)_3P]}_{\text{Triethylphosphine.}} = 2\underbrace{[(C_2H_5)_3PS]}_{\text{Sulphide of triethylphosphine.}} + \underbrace{\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''}_{\text{Dicyanide of ethylene-hexethyl-diphosphonium.}} C_2N.$$

Owing to the low temperature at which the reaction is accomplished, the hydrocyanic acid is not changed in this case, and may be recognised without difficulty by the ordinary reagents. The diphosphonium, which is simultaneously formed, was traced as platinum-salt, exactly in the same manner as the tetrethylphosphonium in the process previously mentioned. The product of the reaction, freed as far as possible from the sulphide by repeated evaporation and ultimately by treatment with ether, was precipitated by dichloride of platinum. The dingy platinum-salt was purified by treatment with sulphuretted hydrogen and reprecipitation. Repeatedly treated in this manner, it assumed the character of a pure compound, which on analysis gave numbers closely agreeing with the formula,



$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2.$$

Since I shall have to give a detailed account of the diphosphonium-compounds in one of the following sections of this inquiry, I need not for the present enter into further particulars regarding this reaction.

In concluding this paragraph, I may append a few remarks upon the deportment of sulphocyanate of triethylphosphonium under the influence of heat. This salt is readily procured by dissolving triethylphosphine in hydrosulphocyanic acid. Submitted to the action of heat, it is partly volatilized without decomposition: the greater portion, however, is decomposed, sulphide and the disulphide-of-carbon-compound of triethylphosphine, together with free disulphide of carbon, appearing among the volatile products of the reaction, while a brown ill-defined substance remains in the retort, yielding when treated with an alkali, an appreciable quantity of ammonia. I have not examined this change in detail, but it is obvious that one of the direct products of the reaction is sulphocyanate of ammonium, the further decomposition of which explains the appearance of the disulphide of carbon as well as the other products observed. The residue, of course, must contain the varied compounds generated by the action of heat on sulphocyanate of ammonium.

Behaviour of the Arsines and Stibines with the Sulphocyanates of Phenyl and Allyl.—The facility with which the compound ureas containing nitrogen and phosphorus are formed, induced me to attempt the production of analogous compounds with arsenic or antimony in place of phosphorus. I therefore treated sulphocyanate of phenyl and oil of mustard successively with triethylarsine and triethylstibine, first at ordinary and then at gradually increasing temperatures in sealed tubes. But not one of these experiments led to the expected result. The arsines and stibines differ, indeed, in their chemical character, much more from ammonia than the phosphines. Their incapability of forming saline compounds with acids is alone sufficient to render the formation of ureas containing arsenic and antimony somewhat improbable. When mixtures of triethylarsine with sulphocyanate of phenyl on the one hand, and sulphocyanate of allyl on the other, were left to stand for some time at ordinary temperatures, the liquid in both cases was found to be traversed by a small quantity of beautiful needle-shaped crystals. The crystals from both mixtures were found to be the same; they were readily identified with the beautiful needles which are gradually formed in triethylarsine when left in contact with atmospheric air.

Behaviour of Triethylphosphine with Cyanates.—The formation of sulphuretted ureas containing phosphorus and nitrogen led me to try whether the corresponding oxygen-compounds could likewise be produced.

When *cyanate of phenyl* is mixed with the phosphorus-base, great heat is evolved, indicating a marked chemical reaction. The mixture on cooling solidifies into a mass of shining crystals which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty even in boiling alcohol. By recrystallization from the last-mentioned solvent, the new body is easily obtained pure. The further examination of the resulting crystals proved, however, that they by no means consisted of the compound urea of which I was in search. From the analysis, which I intend to give in connexion with other researches, it appeared that the crystals still possessed the composition of cyanate of phenyl, that, indeed, they were *cyanurate of phenyl.* The triethylphosphine in this case appears to induce nothing more than a new molecular disposition of the elements in cyanate of phenyl. The peculiar character of this metamorphosis may be perceived in the most beautiful manner by dipping a glass rod moistened with triethylphosphine into a considerable quantity of cyanate of phenyl. The liquid immediately becomes hot, and solidifies after a few seconds into a shining crystalline mass of the cyanurate.

Similar results were obtained by the action of the phosphorus-base on *cyanate of ethyl.* The two bodies may be mixed without evolution of heat, and the mixture does not solidify; but the transformation is soon indicated by the diminution of the penetrating odour of the cyanate. If, as soon as the odour has disappeared, the liquid be mixed with dilute hydrochloric acid, which removes the free phosphorus-base, the oil which floats on the surface quickly solidifies into a solid crystalline mass which, when recrystallized from boiling water, exhibits all the properties of *cyanurate of ethyl.*—When a stream of *cyanic acid* gas is passed through triethylphosphine, the odour of the acid disappears, while the phosphorus-base becomes turbid, and yields a white deposit of *cyanuric acid.*

In connexion with these experiments, I have had occasion to convince myself that *cyanic acid* gas and *phosphoretted hydrogen* do not act upon one another, at least at ordinary temperatures.—I was anxions to ascertain whether the peculiar action of the phosphorus-base on the cyanates extended likewise to the cyanides. I found, however, that *cyanide of methyl* (acetonitrile) or *cyanide of phenyl* (benzonitrile) may be left for days in contact with the phosphorus-base at temperatures varying from 100° to 150°, without experiencing the slightest alteration. Had these substances been changed under the above conditions, like the cyanates, their transformation into methyl- and phenyl-compounds corresponding to cyanethine might have been expected.

Experiments in the Methyl-series.—The information which I have collected with reference to the phosphorus-compounds, has been almost exclusively obtained by the study of triethylphosphine. In exceptional cases only have I worked in the methyl-series. Trimethylphosphine, on account of its volatility, is much less easily prepared than the ethyl-compound, and especially much more difficult to preserve. This body is oxidized with such rapidity, that it disappears from the hand of the operator during manipulation. Its odour, moreover, is insupportable for any length of time.

Nevertheless, I have made a few experiments with the methyl-compound, a slight sketch of which may form the conclusion of this paper.

The phosphorus-derivatives of the methyl-series exhibit the most perfect analogy with the corresponding ethyl-compounds.

Oxide of trimethylphosphine produces with iodide of zinc, with dichloride of platinum, and with trichloride of gold, the homologues of the several compounds obtained from the oxide of triethylphosphine.

When trimethylphosphine, either pure or dissolved in alcohol and ether, is submitted to the action of disulphide of carbon, all the phenomena are reproduced which I have mentioned at some length in describing the corresponding ethyl-base. The red crystals which are formed are somewhat paler, much more volatile, and much more readily altered. The disulphide-of-carbon-compounds of the methyl- and ethyl-series exhibit in their properties the same relation which obtains between the sulphides of the two series.

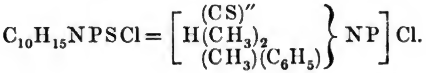
The formula

$$C_4H_9PS_2 = (CH_3)_3P, CS_2$$

was established by analysis.

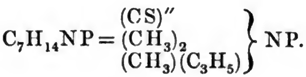
The red crystals are changed with the utmost facility into sulphide of trimethylphosphine. In the hope of forming fine crystals, similar to those obtained with the ethyl-compound, a solution of the red crystals in warm ether was allowed to cool in a tall open cylinder. When the solution was examined next morning, it had become colourless, leaving, upon spontaneous evaporation, the beautiful crystals of the sulphur-compound.

The sulphocyanates of phenyl and allyl readily combine with trimethylphosphine. The reaction is even more powerful than with the ethyl-base. The urea-body, which trimethylphosphine produces with sulphocyanate of phenyl, is a liquid which I have not been able to obtain in the solid state. Directly prepared from the constituents, or separated from one of its crystalline salts, it forms a slightly coloured oily liquid, soluble in water, difficultly soluble in ether, readily soluble in alcohol. On adding concentrated hydrochloric acid to the oil, it gradually solidifies to a crystalline mass of sulphur-yellow delicate, hair-like needles, which may be recrystallized both from water and from alcohol. I have fixed the composition of this phosphoretted urea by a chlorine-determination in a chloride of the composition,



$$C_{10}H_{15}NPSCl = \left[\left.\begin{matrix}(CS)''\\ H(CH_3)_2\\ (CH_3)(C_6H_5)\end{matrix}\right\}NP\right]Cl.$$

The brown liquid which is formed, with considerable evolution of heat, when trimethylphosphine is brought in contact with mustard oil, gradually deposits well-formed transparent colourless prisms, the habitus of which resembles that of the corresponding ethyl-compound. The crystals were not analysed, but there can be no doubt that they were the methylated phosphorus-urea of the allyl-series:



$$C_7H_{14}NP = \left.\begin{matrix}(CS)''\\ (CH_3)_2\\ (CH_3)(C_3H_5)\end{matrix}\right\}NP.$$

Phosphoretted hydrogen is without action on the sulphocyanates of phenyl and allyl.

In conclusion, I beg to thank Drs. A. Leibius and M. Holzmann for their assistance in some of the experiments connected with this inquiry.

XXVI.—*On the Discrepancies in the Statements of Pelouze and F. Mohr, respecting the Solubility of Gallotannic Acid in Ether.*

By Professor Bolley.

For the extraction of tannic acid from coarse gall-nut powder, in his "Displacement Apparatus," Pelouze recommends the use of ordinary, not absolute, ether. The liquid which then runs off, separates into two layers, the lower of which is thickish, while the upper is mobile and less coloured. The lower liquid contains the tannic acid, and is regarded by Pelouze as a solution of tannic acid in water; the upper liquid is stated to be ether, holding in solution small quantities of tannic acid, colouring matter, &c.

Mohr, in his commentary on the Prussian Pharmacopœia, decidedly contradicts this statement. His view of the matter has found its way into most Manuals of Chemistry, articles in Chemical Dictionaries, &c., and is generally received as correct. He regards the lower stratum of liquid above-mentioned as *a concentrated solution of tannic acid in ether*, and the upper, as *ether* which has dissolved only a small quantity of tannic acid. The two layers, he maintains, are not soluble one in the other. If this be so, it affords another example of a condition hitherto known to exist in one instance only (that of coniine), in which the solution of a body in a certain solvent is not diluted by contact with that same solvent. In spite of this anomaly, Mohr's statement has been adopted without experimental verification. Mohr rests his view on an experiment described by himself. On treating tannic acid with anhydrous ether, he obtained the thickish layer already mentioned, and above it there floated a stratum of ether, containing only a small quantity of tannic acid.

I have likewise examined this peculiar phenomenon. I find that *anhydrous ether* (previously decanted several times over chloride of calcium, boiling at 34·9° C., and having a specific gravity of 0·724 at 11·25° C.), takes up but a very small quantity of tannic acid, indeed scarcely any (0·206 p. c. at 5° C.), while the greater part of the tannic acid remains in the liquid in the form of a dry compact powder. On mixing the ether with half its volume per cent. of water, the thickish liquid is formed. The ether—the upper layer—when mixed with a little water, takes up rather more tannic acid than the anhydrous ether. I find that the upper layer—pure ether with 1 vol. p. c. of water—takes up 1.2 p. c. tannic acid.

This result appears to confirm Pelouze's view. It is not however true that the syrupy layer is a concentrated aqueous solution of tannic acid. On carefully removing a portion of this liquid, so that none of the upper stratum may mix with it, introducing it into a retort, and distilling with good condensation, considerable frothing takes place at first, and ether passes over, followed by water, the two liquids forming layers of equal depth in a cylindrical receiver.

If a little water be added to these two liquids, a third layer is formed, which rests between the two, and is therefore insoluble both in ether and in water. This behaviour appears to me to render probable the existence of a chemical compound of tannic acid, ether, and water, possibly an acid ethyl-salt constituted like ethyl-sulphuric acid, that is to say, a *tannate of ether and water*.

There is a practical deduction from these experiments which deserves to be mentioned. The behaviour of pulverized and well dried tannic acid to ether, is so peculiar that it may be used as a test of the presence of water in that liquid. In anhydrous ether the powder remains quite unaltered, but in hydrated ether it cakes together or deliquesces to a thickish syrup, according to the amount of water present, and the quantity of tannic acid added. Very small quantities of tannic acid give a distant reaction.

XXVII.—*On the Colouring Matters of Persian Berries, and on certain general relations of Yellow Vegetable Dyes.*

By Professor Bolley.

The chemical investigations hitherto published respecting Persian Berries (*Yellow berries, graines d'Avignon, Krautzbeeren*) may be epitomized as follows:—

Kane[*] distinguishes two colouring matters: (a). *Chrysorhamnin,* a yellow substance which may be extracted by ether, crystallizes in needles, is nearly insoluble in cold water, but easily soluble in ether. It contains, according to the mean of two analyses, 58·02 per cent. of carbon and 4·70 p. c. hydrogen, and is said to be decomposed by solution in hot alcohol or water and boiling of the solution, yielding another colouring matter (b), called *Xanthorhamnin,* which is soluble in water and alcohol, but insoluble in ether, and when dried at 320° F. contains 52·55 C. and 5·15 H.

Gellatly[†] obtained, with ether, neither chrysorhamnin nor any other characteristic substance, but with alcohol he obtained a yellow substance, crystallizing in needles, easily soluble in water, whether cold or hot, insoluble in ether and containing (when dried at 100° C.) 52·10 % C. and 5·78 H. This body he regarded as xanthorhamnin in a tolerably pure state. It is decomposed by heating with dilute sulphuric acid, yielding, together with glucose, a body called *Rhamnetin,* soluble in water, alcohol, and ether, and containing 59·41 % C. and 4·38 H.

Hlasiwetz,[‡] in his paper on quercitrin, makes some observations on Gellatly's experiments, chiefly, however, with reference to the elementary analyses. The nature of his suggestions may be understood from the following table:—

Percentage of carbon and hydrogen in

Quercitrin at 100° according to Bolley (1841) according to Hlasiwetz (1859)	Kane's Xanthorhamnin.	Gellatly's Xanthorhamnin.
C = 52·49	52.55	52·10
H = 5·03	5·15	5·78
Rigaud's Quercetin.	Chrysorhamnin.	Gellatly's Rhamnetin.
C = 59·23	58·02	59·41
H = 4·13	4·70	4·38

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[*] Phil. Mag., July, 1843, p. 3.

[†] Edinb. New Phil. Jour. vii, 252.

[‡] Ann. Ch. Pharm. cxii, 96.

Hlasiwetz regards xanthorhamnin as identical with quercitrin, and rhamnetin as identical with quercetin, but he has not made any original researches on Persian berries.

With the view of clearing up some of the above-mentioned discrepancies, I have likewise made an investigation of Persian berries. In the first place I must observe that I obtained an abundant extract with *crude ether* (this may perhaps explain the differences between the statements of Kane and Gellatly). This extract, after the ether had been evaporated, the residue taken up by alcohol, the solution filtered, and the alcohol evaporated, with addition of water,—yielded stellate groups of yellow needles, which were not altered by repeated solution, boiling and precipitation.

I analysed two different portions of this substance, and obtained from the one

C = 58·87 per cent.
H = 4·66 „

and from the other which was dried for a longer time at about 120° C.

C = 60·239 per cent.
H = 4·180 „

These crystals are somewhat soluble in pure ether, sparingly in water, easily in alcohol. Their solution gives with *neutral acetate of lead*, a brick-red precipitate; with *nitrate of silver*, a blood-red liquid, and afterwards reduced silver. I found some time ago that the lead precipitate is peculiarly characteristic of quercetin, and I have now to make a similar observation respecting the silver reaction: quercetin behaves both with lead and with silver solutions precisely in the manner just described. The crystallized colouring matter which I obtained by the above process is beyond all question identical with quercetin. The peculiar interest of this fact is that it demonstrates the *pre-existence in a vegetable substance of a product of the decomposition of quercitrin.*

Chrysorhamnin (which Gellatly did not obtain) is perhaps the same as quercetin; but, from the preceding observations, it appears doubtful whether this body can easily decompose and yield a substance like that which Kane describes under the name of xanthorhamnin. If therefore, as Hlasiwetz supposes, rhamnetin is identical with quercetin, it follows that decomposition is not necessary to the production of rhamnetin. Or may it not be possible that this decomposition takes place spontaneously in some kind of yellow berries? Several varieties of these berries are in fact distinguished according to their appearance and their origin. This assumption, which is by no means improbable, may perhaps serve to reconcile some of the contradictions in the statements of Kane and Gellatly.

XXVIII.—*On a hitherto unobserved source of Paraffin.*

By Professor Bolley.

Masses of naturally separated paraffin have been found in deposits of rock-oil, *e.g.*, at Borystow in Gallicia; and Ozokerite, Scheererite, Idrialin, &c., afford proof that hydrocarbons differing considerably in melting point and chemical composition occur ready formed in nature; but paraffin, which occurs in tar and in certain mineral substances used for the production of heat and light, has hitherto been regarded as a product of the action of heat.

In the Technical Laboratory of the Swiss Polytechnic School, researches are at present being made on certain kinds of coal used for the production of illuminating gas; and one result of these researches, easily detached from the rest, I am now about to communicate.

Boghead shale—which, according to Gœppert, is not a true coal—has been examined by several chemists, with reference to the quantity and composition of the residue which it leaves when heated, and the nature of the volatile products. I have endeavoured to ascertain the nature of some of its proximate constituents by exhausting them with various reagents. A kilogramme of pulverized Boghead cannel coal yielded to alcohol 2·14 parts of solid extract residue; and to ether, after drying, 2·63 pts. The alcoholic extract presented less interest than that obtained with ether, which was unctuous to the touch and not very deeply coloured. I found that it could be redissolved in ether, and decolorised by agitation with animal charcoal. After this treatment, however, the residue exhibited by elementary analysis a quantity of oxygen amounting to 11 per cent., and gradually turned yellowish when heated for some time in the water-bath above its melting point. It sustained a slight loss by boiling with soda-lye, and the undissolved portion melted at 41° C, remained colourless when heated, solidified in crystalline laminæ, was insoluble in water, sparingly soluble in alcohol, somewhat more soluble in ether. The analysis of this residue gave

Carbon	86·33	per cent.
Hydrogen	13·32	„
	99·65	

The melting point of paraffin was found by Reichenbach to be 43° C. We know, however, that different samples of paraffin, both natural and artificial, melt, some at higher, some at lower points, so that this circumstance need not prevent us from regarding the substance in question as paraffin.

To me it appears probable that paraffin exists, as such, in several of the materials from the distillation-products of which it has hitherto been prepared, such as peat, shale, lignite, &c., and the process of separation just described affords a convenient method of testing such substances with reference to their utility for the preparation of paraffin, which has hitherto been done exclusively by dry distillation.

I must further remark, that from two sorts of coal which I examined in this way, I obtained, not paraffin, but extracts more of the nature of asphalt. It is commonly stated that the non-existence or the rarity of occurrence of paraffin in coal-tar is attributed to the great heat employed in the distillation. May it not rather be due to the fact that true coal does not contain paraffin ready formed, and therefore cannot yield a tar containing paraffin?

XXIX.—*Note of the Action of Chloride of Ethyl upon Ammonia.*

By Charles Edward Groves.

It has often struck me as remarkable, that while the deportment of ammonia with the bromide and iodide of ethyl had been so carefully studied, the action of this substance upon the chloride of ethyl should scarcely have been noticed. Although the difficulty of manipulating so volatile a substance as chloride of ethyl promised but little advantage in the practical preparation of the ethyl bases; it appeared nevertheless desirable to examine the reaction, in order to complete the history of the formation of these substances. When chloride of ethyl sealed up in stout glass tubes with about three times its bulk of alcoholic ammonia — formed by nearly saturating alcohol with dry ammonia — was digested for six or seven hours at the temperature of 100° C., a large quantity of a white crystalline substance was deposited in the tubes, apparently consisting of chloride of ammonium. The tubes were then opened and the contents thrown on a filter, the white crystalline powder washed with absolute alcohol, and the filtrate evaporated to dryness on the water-bath, to expel alcohol and excess of ammonia. The residue was then dissolved in water, filtered, and submitted in a retort to the action of an excess of oxide of silver, in order to set free the bases formed during the reaction. On heating the mixture, the whole of the volatile bases passed over. The residue in the retort, consisting of oxide and chloride of silver, together with the hydrated oxide of a non-volatile ammonium-base, was thrown on a filter and washed with water until the washings were no longer alkaline. The filtrate neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and filtered, yields with bichloride of platinum, a yellow crystalline precipitate, which was washed with a small quantity of cold water and recrystallized from boiling water.

0·185 grammes of substance yielded 0·0545 grammes of platinum; this shows a percentage of platinum equivalent to 29·4 per cent. The formula—

$$(C_4H_5)_4NClPtCl_2$$

requires 29·44 per cent. of platinum. The non-volatile base produced in the reaction between chloride of ethyl and ammonia, is therefore, as might have been expected, the hydrated oxide of tetrethylammonium. The alkaline distillate, containing the volatile portion of the bases was neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and precipitated with an insufficient quantity of bichloride of platinum. The precipitate, consisting of thin crystalline hexagonal plates, was recrystallized from a small quantity of water, to which it was found convenient to add a few drops of alcohol, the salt being rather insoluble in dilute alcohol.

0·235 grammes of substance gave 0·092 of platinum.

The formula—

$$[(C_4H_5)\ H_3N]\ Cl,\ Pt\ Cl_2$$

requires 39·29 per cent. of platinum and the analysis gave 39.15 per cent.

This result shows the existence of ethylamine among the volatile products of the action of chloride of ethyl upon ammonia.

By successive partial precipitations and recrystallizations, a considerable quantity more of the platinum-salt of ethylamine was separated; until at last a very small quantity of another and more soluble salt was deposited from the mother-liquors. After a single recrystallization, which was all that was possible, owing to the amount being so small, it was dried and analysed; and although some crystals of the ethylamine platinum-salt could be discerned by the microscope, it gave results which approximated closely with the theoretical percentage of the diethylamine platinum-salt.

0·170 of substance gave 0·062 of platinum;

this gives a percentage of 36·47 of platinum.

The formula—

$$[(C_4H_5)_2H_2\ N]\ Cl,\ PtCl_2$$

requires 35·35 per cent of platinum. The above platinum determination might also represent a mixture of the salt of ethylamine and triethylamine; but the compound analysed, although more soluble in water than the ethylamine-salt, was not nearly so soluble as the salt of triethylamine; moreover the latter substance is easily recognised by its crystalline form. In addition to the salts above mentioned, a small quantity of triethylamine was, in all probability, present among the products of the reaction of chloride of ethyl upon ammonia; but owing to the small proportion in which it existed, and the known solubility of its platinum-compound, I have not been able to establish its formation by experiment.

The following equations represent the action of chloride of ethyl upon ammonia:—

$$\begin{aligned} H_3N + C_4H_5Cl &= [(C_4H_5),H_3N]\ Cl \\ 2\,H_3N + 2C_4H_5Cl &= [(C_4H_5)_2H_2N]\ Cl + H_4NCl \\ 4\,H_3N + 4C_5H_5Cl &= [(C_4H_5)_4\ \ N]\ Cl + 3H_4NCl. \end{aligned}$$

The experiments which I have described show a marked difference in the action of the chloride when compared with that of the bromide and iodide of ethyl. The chloride of ethyl produces almost exclusively the chloride of ethylammonium, together with small quantities of the chlorides of diethylammonium and tetrethylammonium. The bromide of ethyl, according to the experiments of Dr. Hofmann, gives chiefly the bromide of ethylammonium, but also very appreciable quantities of the bromides of diethyl- and triethylammonium, with but a small proportion of the tetrethylammonium-compound; and lastly, the iodide produces the three volatile bases in about equal proportions, but generally very appreciable quantities of the tetrethyl-ammonium-compound.

The above experiments were performed in the Laboratory of Dr. Hofmann.

XXX.—*On the Crystalline Form of Metallic Chromium.*

By Professor Bolley.

The preparation of sesquichloride of chromium and of crystallized metallic chromium by the methods recently given by Wohler,[*] is very easy. I entrusted the preparation to one of the students in my laboratory, who obtained a product exhibiting the colour and lustre of the crystalline powder described by Wöhler. Wöhler says of this substance—"It exhibits, even with a magnifying power of 50, crystalline aggregations having the form of fir-branches interspersed with very beautiful *Rhombohedrons* of great lustre and nearly tin-white colour." I have examined the crystalline mass with a magnifying power of 85, and have found that it contains numerous fir-shaped arboresences such as Wöhler describes. But it was immediately apparent that the loose crystals dispersed through the mass were referable, not to rhombohedral but to octohedral primary forms. These crystals are *very frequently* united in groups of four, in the shape of a cross, but the smallness of the crystals precluded the possibility of measurement. My colleague, Professor Kenngott, has had the goodness to determine the form of these crystals, and finds that they are octohedrons belonging to the quadratic system. They are for the most part octagonal pyramids *p*, *p*, combined with a more acute pyramid *s*, and a more obtuse pyramid *o*. The *p*-faces are very deeply striated; the *o*-faces very smooth and shining.

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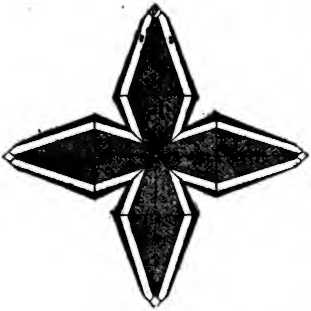
[*] Leichte Darstellungsweise des metallischen Chroms. (Ann. Ch. Pharm. cxi, 230.)



It is well known that the crystalline forms of the metals belong chiefly to two systems, the ductile metals crystallizing in the tesseral, the brittle metals in the rhombohedral system, while some are dimorphous, and exhibit forms belonging to both these systems. Hitherto *tin* is the only metal known to crystallize in another system, viz., the quadratic. *Boron* likewise, according to Quintino Sella,* crystallizes in the quadratic system.

Chromium affords, therefore, the third example of an elementary body, differing from most others in its crystalline form. It follows also from these observations, that although certain compounds of chromium are isomorphous with the analogous compounds of iron, this isomorphism does not exist in the metals themselves.

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* Sulle forme cristalline di alcuni sali di platino e del Boro adamantino, par Quintino Sella. Torino, 1857.

XXXI.—*On a new Lead-salt, corresponding to Cobalt-yellow.*

By S. D. Hayes, Edinburgh University.

In the course of some investigations on the cobalto-cyanide compounds, I was obliged to use a quantity of cobalt-yellow, the pigment discovered by M. Saint Evre, in 1852.* All the methods described for preparing this salt are very tedious, so that it became an object to find a more ready means. The best method hitherto given, is to precipitate a solution of nitrate of cobalt with an excess of potash; then by passing a current of deutoxide of nitrogen (NO_2) through the mass, the cobalt-yellow is obtained: but the greater part of the deutoxide passes through without being absorbed; the experiment requires hours; and the amount of salt obtained is very small.

As the composition of this body is considered doubtful, it occurred to me that it might be made from peroxide of nitrogen (NO_4), and after a few trials I obtained it very readily, in large quantities, and found that all the cobalt contained in a solution may thus be converted into cobalt-yellow. Two bottles, connected and supplied with funnel tubes, are about half filled with a solution of nitrate of cobalt, to which potash, slightly in excess, is added. On passing a brisk current of peroxide of nitrogen through the liquid, the mass in the first bottle soon changes colour, and the pigment begins to fall; by adding small quantities of potash, occasionally, through the funnel-tubes, all the cobalt may be removed. The peroxide of nitrogen is most readily prepared by allowing a current of the deutoxide, produced from copper and nitric acid, in a small flask, to mix with a current of common air from a gasometer, in a dry empty bottle, before passing into the cobalt-solutions. The current of air can be regulated at the gasometer, and the flask for generating the deutoxide can be easily removed and replenished when necessary. A solution of the carbonate may be used instead of caustic potash, for precipitating the cobalt-solutions, with the same results.

A. Stromeyer, when working upon this salt, endeavoured to obtain an analogous body with lead; he succeeded in getting a yellow solution by means of nitrite of potash and acetic acid, in a solution of lead, but he then added cobalt which gave a precipitate.*

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* Ann. Ch. Phys., [3], xxxviii, 177.

On treating a solution of nitrate of lead with potash, and passing a current of peroxide of nitrogen through the liquid, precisely as in making the cobalt-yellow, I found that all the peroxide was absorbed, and as the oxide of lead disappeared, the solution became very yellow. Evaporating and crystallizing this, I obtained large yellow prismatic crystals; nitrate of potash crystallizes at the same time, and if the peroxide of nitrogen has been passed through the lead too long, nitrate of lead is formed.

The yellow salt was easily separated and recrystallized. The bases were determined as sulphates, in the analyses, with the following results:—

I. 0·7462 grms. pure salt gave 0·4200 grms. sulphate of lead and 0·0097 grms. lead = 0·319493 grms. oxide of lead, and 0·2472 grms. sulphate of potash = 0·133545 grms. potash.

II. 1·4590 grms. gave 0·6387 grms. oxide of lead and 0·25931 grms. potash.

III. 1·0271 grms. gave 0·43745 grms. oxide of lead and 0·1881 grms. potash.

The nitrogen was determined as gas, metallic copper reduced from the *fine* oxide, being used in the combustion tube with a little oxide at the fore end. The gas was collected and washed in a small apparatus, then transferred to the eudiometer, where it was measured.

I. 0·1926 grms. salt, gave 45·6277 cubic centimeters nitrogen at temperature 6·0°C.; and pressure 277·5 millimeters = 16·30 cc., at 0°C. and 760 mil. pressure, = 0·204822 grms.

II. 0·1958 grms. gave 16·23 cc. at 0°C. and 760 mil. pressure, = 0·225983 grms.

The water was determined by combustion with metallic copper.

I. 0·7834 grms. gave 0·0274 grms. water.

II. 0·9145 grms. gave 0·0314 grms. water.

III. 0·4735 grms. gave 0·0177 grms. water.

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* Ann. Ch. und Pharm., xcvi, 228.

	I.	II.	IIII.	IV.
Oxide of lead . . .	42·81	43·08	42·59	43·22
Potash	17·90	17·77	18·31	„
Nitrogen	10·63	„	10·35	„
Water	3·47	3·43	3·73	„
Oxygen by difference	25·16	„	25·02	„
	100·00		100·00	

The above analyses correspond to the following calculated formula:—

PbO . . .	111·56	42·98
KO . . .	47·00	18·10
N_2	28·00	10·78
O_8	64·00	24·67
HO . . .	9·00	3·47
	259·56	100·00

As this salt crystallizes out with nitrate of potash, it is of about the same degree of solubility, in either hot or cold water, and the solution may be boiled for some time without any decomposition, but it is readily decomposed by sulphuric, hydrochloric, or nitric acid, giving off red fumes. With the common reagents, it acts like nitrate of lead, but with a solution of sulphate of cobalt, it gives cobalt-yellow, which goes down with the sulphate of lead. It loses its atom of water at 100°C., but if the temperature be raised a few degrees higher, the red fumes come off abundantly. The crystals are of a bright yellow colour, and remain unaltered in the air.

I am not yet prepared to give my salt any decided *rational* formula, but its composition may be expressed in several ways as below. When $2NO_4$ is passed over 2KO, we get $KONO_5$ and $KONO_3$, two distinct salts; but if $2NO_4$, be passed over CoO and KO, as in the case of cobalt-yellow, or over PbO and KO, as in this salt, we get only one salt of a double composition, which we may write in like manner:

$$KONO_3, CoONO_5, \text{ or}$$
$$KONO_3, PbONO_5 + HO.$$

But there is an objection to this, as cobalt-yellow is almost insoluble in water. These salts may also be looked upon as double peroxides, in which two equivalents of oxygen have been replaced by two equivalents of NO_4, thus

$$\left\{\begin{matrix} PbO, NO_4 \\ KO, \ NO_4 \end{matrix}\right\} + HO;$$

but from the nature of the salts I hardly think that NO_4 exists in them. However Gmelin describes a salt to which he gives the formula $2PbO, NO_4$, aq.,[*] and we express the composition of these salts, just as well, by writing them thus,

$$KONO_4, CoONO_4; \text{ or}$$
$$KONO_4, PbONO_4 + HO.$$

This subject will be pursued, and I hope to get several other salts, which must give some reactions that will lead to the right rational formula.

These experiments were made in the laboratory of the Edinburgh University.

XXXII.—*On the Electrolytic Test for Arsenic, and on the Presence of that Metal in certain Reagents.*

By Charles L. Bloxam.

In a former communication upon this subject which I had the honour of presenting to the Society,[†] it was shown that when a solution containing arsenious acid is mixed with diluted sulphuric acid and subjected to the action of the voltaic current, arseniuretted hydrogen is evolved at the negative terminal, and that in this way very minute quantities of arsenious acid can be detected with great certainty, even in the presence of large quantities of organic matter, and without adding any material to the liquid which would interfere with its examination by other analytical processes. It was also stated that arsenic acid did not respond to this test, and that the presence of mercury in the liquid interfered very materially with the detection of the arsenic.

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[*] Handbuch. Bd. 3, s. 142.

[†] See page 12 of this volume.

It is the object of this paper to show how arsenic acid may be brought within reach of this test, how the interference of mercury may be prevented, and how all chance of error due to the evolution of antimoniuretted hydrogen may be avoided.

The form of apparatus recommended in the previous notice admitted of some obvious improvements. A tube-funnel has been added, to permit the introduction of the liquid to be tested, and the platinum wires communicating with the battery have been replaced by broad strips of platinum foil.

If arsenious acid be converted into arsenic acid by boiling with hydrochloric acid and chlorate of potassa, and the solution be poured into the diluted sulphuric acid during the passage of the current, no arseniuretted hydrogen is evolved; but if a few drops of solution of sulphurous acid or of bisulphite of soda be poured down the funnel-tube, a greenish yellow iridescent crust of tersulphide of arsenic is almost immediately deposited at a little distance beyond the heated portion of the tube, and is followed, in most cases, by the usual mirror of metallic arsenic.

Since arsenic acid is reduced with great difficulty by sulphurous acid at the ordinary temperature, it appeared probable that the effect was really due to the hydrosulphuric acid formed by the action of the nascent hydrogen upon the sulphurous acid, and accordingly it was found that the introduction of a few drops of solution of hydrosulphuric acid into the electrolytic cell also caused the evolution of arseniuretted hydrogen.

If an excess of hydrosulphuric acid be employed, a deposit of sulphur is formed in the tube, nearer to the orifice than the deposit of sulphide of arsenic, from which it may be very easily distinguished by its much lighter colour, and by its insolubility in a warm solution of sesquicarbonate of ammonia, which readily dissolves the sulphide of arsenic.

Three experiments may be especially referred to in evidence of the certainty attending this process.

0·01 grn. of arsenious acid was boiled with hydrochloric acid and chlorate of potassa, and introduced into the electrolytic apparatus, and the reduction-tube through which the hydrogen escaped was heated to redness for 30 minutes without any appearance of deposit; but, on adding 5 grn. measures of a solution of bisulphite of soda, a yellow crust of tersulphide of arsenic made its appearance in 5 minutes, and was followed by a distinct deposit of metallic arsenic, identified by its volatility and its solubility in chloride of lime.

In a second similar experiment, 10 grn. measures of a saturated solution of hydrosulphuric acid were poured down the funnel-tube, instead of the bisulphite of soda. The crust of sulphide appeared within 10 minutes, and that of metallic arsenic within 15 minutes.

A third experiment was made with only 0·001 grn. of arsenious acid which had been boiled with hydrochloric acid and chlorate of potassa; within 13 minutes after the addition of 10 grn. measures of hydrosulphuric acid, the yellow sulphide of arsenic appeared in the tube.

It was found that however large a proportion of hydrosulphuric acid was poured into the decomposing cell, the arsenic was still evolved, the metal combining with the nascent hydrogen in preference to the sulphur. It appeared probable, however, that the addition of hydrosulphuric acid would at once precipitate any antimony or mercury present in the liquid under examination, and would prevent their interference with the detection of the arsenic.

One grain of tartar-emetic (0·36 grn. Sb) dissolved in water, was slightly acidulated with sulphuric acid, mixed with an excess of hydrosulphuric acid, and poured, without filtering, into the decomposing cell in which the diluted sulphuric acid was undergoing electrolysis; the evolution-tube was maintained at a red heat for 38 minutes without any deposit in the tube except a thin film of white sulphur.

Another grain of tartar-emetic was then mixed with 0·01 grn. of arsenious acid, which had been boiled with hydrochloric acid and chlorate of potassa, and the mixture was treated with an excess of hydrosulphuric acid, and poured into the same decomposing cell without interrupting the experiment. In 5 minutes, yellow rings of tersulphide of arsenic made their appearance in the capillary reduction-tube; in less than 15 minutes, a distinct crust had formed, presenting exactly the same appearance as if no antimony whatever had been present. No deposit had been formed upon the negative plate.

In the next trial, only 0·001 grn. of arsenious acid was mixed with 1 grn. of tartar-emetic; the solution was boiled with hydrochloric acid and chlorate of potassa, diluted to one fluid ounce with water, saturated with hydrosulphuric acid gas, and poured, with the suspended precipitate, into the decomposing cell. Within 15 minutes, a distinct deposit of metallic arsenic was obtained, which dissolved immediately in solution of chloride of lime.

When 1 grn. of tartar-emetic and 0·01 grn. of arsenious acid were mixed with considerable quantities of bread, milk, and beer, and the brown treacly liquid obtained by boiling with hydrochloric acid and chlorate of potassa, and subsequent evaporation, was mixed with excess of hydrosulphuric acid and poured into the decomposing cell, deposits of metallic arsenic and of the tersulphide were almost immediately formed in the tube. On collecting the dark precipitate after the operation, it was easily identified as sulphide of antimony.

In a second experiment of this description, one-fourth of the brown fluid (containing 0·09 grn. Sb and 0·0025 grn. AsO_3) was introduced into the decomposing cell without adding hydrosulphuric acid, when a very distinct mirror of antimony was, of course, formed in the reduction-tube, and a deposit of that metal was obtained on the negative plate. The reduction-tube was then changed, and hydrosulphuric acid added, when deposits of arsenic and its sulphide, free from antimony, were formed in the tube.

To prove that with this modification of the test, the presence of mercury no longer prevented the detection of arsenic, experiments precisely similar to those above described were made, respectively, upon mixtures of 1 grn. corrosive sublimate with 0·01 grn. arsenious acid, and 0·25 grn. corrosive sublimate with 0·0025 grn. arsenious acid, mixed with white of egg, bread, milk, and beer, when no difficulty whatever was found in the detection of the arsenic.

The solution containing chloride of mercury and arsenic acid was electrolytised for half an hour without the slightest appearance of arsenical deposit in the heated tube, the mercury being deposited abundantly upon the negative plate; but on the addition of solution of hydrosulphuric acid, a crust of metallic arsenic was soon obtained.*

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* It will be evident that this method of converting the arsenic into arsenic acid and precipitating the antimony and other metals by hydrosulphuric acid, in the *cold*, may be employed with advantage in Marsh's test; the solution containing the arsenic acid must be filtered, however, before introduction into the evolution bottle, as the suspended sulphide of antimony was found to be immediately decomposed in

In order to ascertain whether the occurrence of putrefaction in an organic mixture containing arsenious acid would interfere with its detection by the electrolytic test, an experiment was made with 0·001 grn. of arsenious acid mixed with meat, white of egg, beer, bread, and milk, and allowed to putrefy for nearly twelve months. No difficulty was experienced in detecting the arsenic.

I am very desirous of convincing myself that reliance may, in all cases, be placed on this process for the detection of arsenic, by operating upon organic matters *exactly similar* in their nature and quantity to those often submitted to the chemist in judicial inquiries, but have hitherto been unable to do this, in consequence of the difficulty of procuring hydrochloric acid so pure that, when examined in the large quantity required for the disintegration of considerable masses of viscera, it did not afford any indication of the presence of arsenic. Believing that I possessed a quantity of sulphuric acid perfectly free from arsenic, I employed it for the preparation of hydrochloric acid; but even this sample was not found to be absolutely free from the impurity, and on resorting to the sulphuric acid, the examination of a large quantity at once proved the presence of a very minute proportion of arsenic, which was more easily traced in the hydrochloric acid, since the latter could be employed without inconvenience in larger quantity, both in the electrolytic and in Marsh's test. The production of sulphuric acid absolutely free from arsenic is now engaging my attention.

It has also been incidentally noticed in the course of these experiments, that various samples of solution of potassa and of the solid hydrate contained very notable quantities of arsenic, attributable probably to their having been prepared from nitre by the action of (arsenical) copper at a high temperature.

A more important point for the consideration of the analytical chemist is the occurrence of arsenic in the hydrosulphuric acid,

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contact with zinc and sulphuric acid. In a mixture containing a grain of tartar-emetic and one-hundredth of a grain of arsenious acid, the latter was detected as easily as if no antimony had been present, by boiling with hydrochloric acid and chlorate of potassa, precipitating the cold solution with excess of hydrosulphuric acid, filtering, and pouring into Marsh's apparatus.

In Marsh's test, the use of electrolytised zinc was found to be attended with advantage in minute investigation, on account of the very slow and steady evolution of gas.

prepared in the usual manner from sulphide of iron and diluted sulphuric acid. On passing the gas for 10 or 15 minutes through a reduction-tube heated to redness, a distinct crust of sulphide of arsenic was formed nearer to the heated portion than the deposit of sulphur. That the crust really consisted of sulphide of arsenic was proved by its solubility in carbonate of ammonia, and by its furnishing metallic arsenic when fused with carbonate of soda and cyanide of potassium in a current of carbonic acid. This experiment was repeated, with the same results, upon different samples of sulphide of iron and sulphuric acid. That the arsenic was due to the sulphide of iron, was ascertained by employing only so much of the purest sulphuric acid as gave no indication of arsenic in Marsh's process. Water saturated with the gas, when examined by Marsh's and the electrolytic test, was not found to contain arsenic.

No arsenic was detected in the washed hydrosulphuric acid gas prepared from native sulphide of antimony and hydrochloric acid.

On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and other Gases.

By Thomas Andrews, M.D., F.R.S., M.R.I.A., and Peter G. Tait, M.A.

(From the Philosophical Transactions for 1860.)*

1. The molecular changes produced by the electric current, or discharge, in certain compound bodies through which it is transmitted, furnish some of the most interesting examples of the action of a decomposing force that have been discovered in later times. The discharge of the Leyden jar, through fine wires or thin metallic leaves, exhibited long ago the heating power of the current, and the interesting experiments of the Dutch chemists afterwards showed that the disruptive discharge has the power of splitting up compound bodies into their constituent parts. The great invention of the pile of Volta, by furnishing an abundant supply of electricity of moderate tension, led subsequently to the important discovery of the polar decomposition of water and of other compound bodies. In the case of gases, it has been known, since the time of Priestly and Cavendish, that the spark-discharge has the apparently antagonistic properties of causing decomposition in some cases and combination in others. Finally, in our own day, Schönbein made the fine observation that a new substance (ozone), alike remarkable for the activity of its properties and for the facility with which it is destroyed, is formed by the action of the spark on pure oxygen gas, in the electrolysis of water, and in certain cases of slow oxidation.

Our object in the present communication is to continue the investigation, already begun by one of us,† of the properties of ozone, by subjecting it under varied conditions to a series of careful volumetric experiments. We hoped, in this way, to throw some new light on the relations of this singular body to oxygen, by determining whether any, and what, change of volume occurs in its formation. Our expectations in this respect have not been disappointed. We have ascertained that when oxygen changes into ozone, a great condensation takes place; so great indeed, that it is almost incompatible with the existence of ozone as an allotropic form of oxygen in the gaseous state. This investigation has naturally extended itself to an examination of the effects produced by the electrical discharge upon other gases, simple as well as compound; and although, from its great extent, this part of the inquiry has as yet been only partially entered into, some of the results already obtained are of considerable interest, and will be referred to in the present communication.

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* The substance of this paper was delivered as a Discourse to the Members of the Chemical Society of London by Dr. Andrews.

† Philosophical Transactions, 1856, p. 1, or Quarterly Journal of the Chemical Society, ix, 168.

Before proceeding further, we must draw attention to the difference of action which, in many cases, we have found to exist between the spark, or spark-discharge, and the glow, or silent discharge. When the former terms are employed in this paper, they indicate a succession of brilliant sparks between two fine platinum wires, usually at the distance of 20 millims, (0·8 inch) from each other, and hermetically sealed into the tube containing the gas under observation. This form of discharge was obtained by connecting the free end of one of the platinum wires with an insulating stand, provided with a brass ball which was brought within a short distance of the prime conductor of an electrical machine in high order, while the free end of the other platinum wire was in connection with the ground. The silent discharge presented no visible character except a faint glow, not visible by daylight, at each metallic point, and was obtained by connecting the first platinum wire, not with the insulator, but directly with the prime conductor. To avoid the mixture of the "brush" with the silent discharge, it was necessary to establish the connection firmly both with the conductor and with the earth wire; and, in some cases, where a full effect was required, the machine had to be turned very slowly.

The electrical machine employed was a small plate one (18 inches in diameter), screwed down firmly to the floor of the apartment, opposite to an open fire. On the prolongation of the axis of the plate, a wheel, 6 inches in diameter, was fixed, from which a belt passed to an iron wheel, 40 inches in diameter, revolving in a wooden frame, which was also fastened to the floor. By this arrangement, the machine could be easily made to turn at the rate of 350 revolutions per minute. To maintain a regular and powerful stream of electricity at this rapid rate of motion, it was found necessary, in addition to the ordinary cushions, to hold with the hand against the plate a rubber covered with amalgam. When in ordinary working order, the machine gave above 600 sparks per minute, and in decomposing water produced in the same time 0·0002 cub. cent. of the mixed gases.*

The ordinary forms of eudiometrical apparatus were found to be wholly inapplicable to this inquiry. We failed in discovering, by their means, whether even a change of volume occurs, when ozone is produced from oxygen. To increase the difficulty, the experiments could not be carried on in presence of mercury or water, as the former is immediately attacked by ozone; and the latter not only destroys it rapidly by contact, but introduces a disturbing cause, in the form of aqueous vapour, exceeding in general the whole effect to be measured. In the apparatus now to be described these difficulties were overcome, and very minute changes of volume determined with certainty.

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* Reports of the British Association for 1855, Trans. of Sect. p. 46.

In figs. 1 and 2, the vessel in which the oxygen was contained is represented of different forms. It consists of a cylindrical tube *ab*, having two fine platinum wires hermetically sealed in opposite sides, and terminating in a capillary tube *cde*, of the form represented in the figure. The liquid in the limbs *d e*, is hydrated sulphuric acid (HO, SO_3), and it is by the changes in the level of this liquid that the alteration in the volume of the gas in *abc* is determined. In order to make the necessary corrections for changes of temperature and pressure, during the interval between two observations, a vessel filled with dry air, of the same form and size as that employed in the experiment, was read along

Fig. 1.

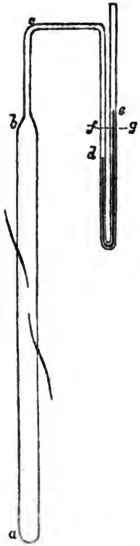


Fig. 2.

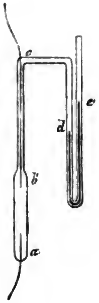
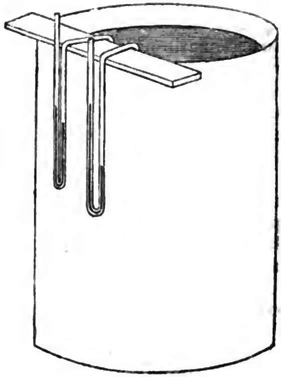
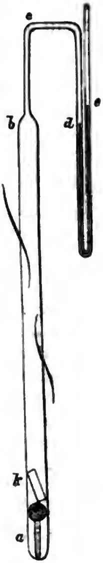


Fig. 3.



with it; the reservoirs of both vessels being immersed in a large calorimeter, as shown in fig. 3. To the first of these vessels, we usually gave the name of *primary* vessel, and to the second that of *auxiliary* vessel. In order to correct for any slight difference in the size of the vessels, or in the diameters of the capillary tubes, simultaneous readings of both were made at different temperatures, and a coefficient thus determined, by means of which the indications of the two vessels could be afterwards accurately compared. When the reservoirs were large, the corrections so to be applied were frequently less than the errors of observation.

Fig. 1°.



The extreme delicacy of this apparatus will be evident from the following considerations. If we take the case of a vessel with a large reservoir (fig. 1°), the changes in volume of the contained gas, supposing the temperature to remain constant, will be nearly proportional to the changes of pressure indicated by a barometer filled with sulphuric acid. As the height of such a barometer, at the mean pressure of the atmosphere, would be about 5500 millims., an alteration of 1 millim. in the difference of levels of the acid in the siphon tube (*de*, fig. 1) would correspond to a change of volume of about $\frac{1}{5000}$th of the entire gas; but, as it was easy to read to 0·5 millim., or even to 0·25 millim., the apparatus in this form enabled us to estimate a change of volume not exceeding one-half, or even one-fourth of that quantity. With a smaller reservoir (fig. 2), the indications of the apparatus were, it is true, not quite so delicate, and a careful set of comparative readings with the auxiliary vessel was always required; but even here, a change of volume amounting to not more than $\frac{1}{5000}$th of the whole, could be determined with certainty.

The absolute change of volume of the gas, corresponding to a given change in the levels of the acid in the siphon tube (corrected in the first instance by the aid of the auxiliary vessel), was estimated in two ways; first, by observing the change of level produced by raising or lowering the temperature of the water in the calorimeter through a small number of degrees; and secondly, by accurately determining, at the end of the experiment, the capacity of the reservoir and that of the capillary tube.

The form of apparatus now described can only be employed when the entire change of volume of the gas does not amount, in the course of the experiment, to more than about one-tenth of the whole. When large changes of volume occur, the free end of the siphon tube must be hermetically sealed, so as to include a certain quantity of air, from whose subsequent change of volume that of the gas in the reservoir can be readily calculated. This modification of the apparatus we have found to be very convenient in experiments upon the action of the spark and silent discharge on the compound gases.

2. The oxygen gas employed in the following experiments was prepared from fused chlorate of potash, and, to purify and dry it, was passed through two U-tubes, the first containing fragments of marble moistened with a strong solution of caustic potash, the second, fragments of glass moistened with sulphuric acid. The potash-tube was sometimes suppressed. In order to remove every trace of nitrogen, the whole apparatus was placed in connexion with a good air-pump, and a vacuum produced to the extent of at least half an inch, while the gas was still being evolved from the fused chlorate (fig. 4). When the process of exhaustion was discontinued, the gas soon filled the apparatus, and was expelled through the mercury at the lower end of the long gauge. The operation of exhausting and refilling the vessel was performed three times in every experiment. Supposing the connexions of the apparatus to have been perfectly air-tight, the nitrogen remaining after this triple exhaustion, could not have amounted to more than $\frac{1}{200,000}$th of the whole. This degree of accuracy was not, it is true, realized in practice, but the oxygen gas, prepared in this way, did not contain $\frac{1}{1000}$th of its volume of nitrogen. The connexion with the air-pump at *a* having been broken (the gas still continuing to pass freely over), the end of the tube was softened in a lamp and bent downwards at an obtuse angle, so as to allow it to dip into sulphuric acid contained in a small dish, as shown

Fig. 4.

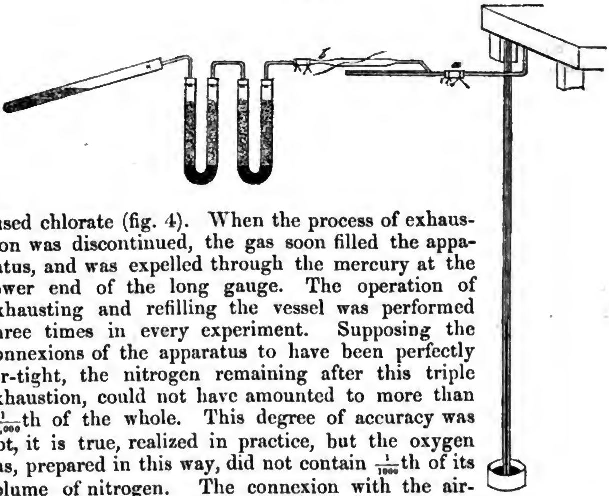
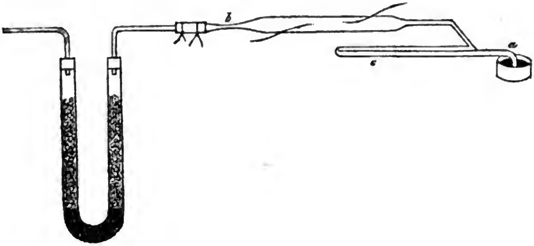


Fig. 5.



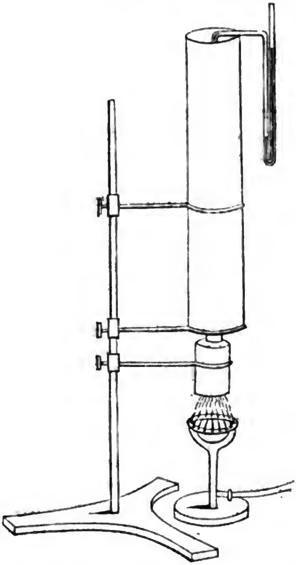
in fig. 5. The current of gas was now arrested, by removing gradually the lamps from the chlorate of potash, so as to allow the apparatus to cool slowly. When the acid had ascended a short way in *a c*, the vessel was sealed hermetically at *b*, and, after the acid had ascended to about the point *c*, the vessel was removed, and placed in the upright position represented in figs. 1 and 2. It was sometimes necessary to expel a bubble or two of gas, in order that the column of acid in the siphon tube might be in a convenient position when the vessel was placed in the calorimeter.

Previous to filling the vessels, they were always cleaned by means of boiling nitric acid, and subsequent washing with distilled water. They were afterwards carefully dried. To the success of several of the following experiments, this precaution was indispensable.

An auxiliary vessel having been filled in the same manner, either with air or with oxygen, the two vessels were placed in the calorimeter (fig. 3), and the difference of the levels of the acid in each carefully read. In our earlier experiments we generally used a cathetometer for this purpose, but latterly we found it more convenient and sufficiently accurate to apply to the limbs of the siphon tubes a scale divided into millimetres. From the rapidity indeed with which the readings were thus made, the results were found to be fully as trustworthy as those obtained with the cathetometer. When quantitative determinations were required, the temperature of the water in the calorimeter and the height of the barometer were carefully noted. After the levels were read, the free ends of the siphon tubes in both vessels were hermetically sealed. The primary vessel was then removed from the calorimeter and placed in connexion with the electrical machine, to be exposed to the action either of the spark or silent discharge. When this operation was finished, the vessel was replaced in the calorimeter, the siphon tubes were opened, and the levels of the acid in the two vessels again read.

In order to examine the effects of heat, the reservoir of the vessel was placed in a sort of air-bath, formed by suspending a long copper cylinder above a LESLIE's gas-burner, the siphon tube being outside the cylinder, fig. 6. In this way a temperature of 300° C., which was sufficient to destroy in a short time all the ozone reactions, was readily obtained. This temperature was estimated without difficulty, by observing the amount of compression of the air in the outer leg of the siphon tube. Our apparatus, with a slight modification, might, in fact, be employed as a thermometer for all temperatures below that at which glass begins to soften.

Fig. 6.



It will probably tend to perspicuity, if we state, before going further, some of the general results of our experiments on the action of the electrical discharge on pure oxygen.

I. When the silent discharge is passed through pure and dry oxygen, a contraction takes place. This contraction proceeds, at first rapidly, but afterwards more slowly, till it attains a limit, which, in one of our experiments, amounted to $\frac{1}{12}$th of the original volume of the gas.

II. If a few electrical sparks be passed through the gas in this contracted state, it expands till it recovers about three-fourths of the contraction; but, however long the sparks are passed, the gas never recovers its original volume.

III. When electrical sparks are passed through pure and dry oxygen, it contracts, but to a much smaller extent than when acted on by the silent discharge. The oxygen is, in fact, brought to the same volume as when electrical sparks are passed through the same gas, previously contracted by the silent discharge.

IV. When oxygen, contracted either by the silent discharge or by sparks, is exposed for a short time to the temperature of 270° C., it is restored to its original volume, and, on opening the vessel, the ozone reactions are found to have disappeared.

The following experiments, taken from a large number which gave similar results, will serve to illustrate the foregoing statements.

a. In a vessel, whose reservoir had a capacity of 5 cub. cent., sparks were passed for ten minutes, and produced a contraction of 5·9 millims., as measured by the change of levels of the acid in the siphon tube. By heating the vessel afterwards to 300° C., the levels were restored to within 0·1 millim. of their original position.

With the silent discharge in the same vessel, a contraction of 39·5 millims. (corresponding to about one-thirtieth of the volume of the gas) was obtained in ten minutes. Of this contraction heat restored 38·7 millims. This slight difference of 0·8 millim. is probably due to distortion of the vessel produced by heat.

Again, the silent discharge gave in ten minutes a contraction of 37·6 millims., of which sparks, subsequently passed for seven minutes, destroyed 29·7 millims., leaving 7·9 millims. undestroyed.

β. In another vessel having a reservoir of the capacity of 0·8 cub. cent., active sparks gave, in fifteen minutes, 4 millims. of contraction. After fifteen minutes more of sparks there was no additional contraction.

The silent discharge was now passed for fifteen minutes, and increased the contraction to 20 millims.; in fifteen minutes more, the entire contraction was 31 millims. Four strong sparks reduced this to 22·5 millims., six or seven more to 16 millims., seven more to 11 millims., and sparks, continued for ten minutes, left 4 millims. of permanent contraction.

γ. In a third vessel, of about the same capacity as the last, sparks gave a final contraction of 7·5 millims.; while the silent discharge, pushed to its limit, increased the contraction to 90 millims. corresponding to about one-twelfth of the entire volume of the gas. This contraction was almost exactly destroyed by heat.

Before leaving this part of the subject, we should mention that, when a full contraction is obtained by means of the silent discharge, it will be found very slowly to diminish from day to day. We have not ascertained whether, at the end of a very long period of time, the original volume of the gas would be recovered. At 100° C., the contraction diminishes much more rapidly than at ordinary temperatures. Thus it appears that the state produced by the electrical discharge is not permanent, even at common temperatures, and that it becomes more unstable as the temperature rises, till at 270° C. it is rapidly destroyed.

We next proceeded to examine the volumetric changes which occur when oxygen contracted by the electrical discharge, is brought into contact with other bodies.

The first body we tried was *mercury*, the physical changes produced on which by ozone are known to be very remarkable. When a capsule containing this metal is broken in a tube of oxygen gas through which the silent discharge has been passed, the mercury instantly loses its mobility, and, if gently shaken, covers the interior of the tube with a brilliant mirror. As the action continues, the mirrored surface breaks up, and the coating becomes converted into a blackish semipulverulent substance. Unless the tube be very violently shaken, the ozone reactions will not be entirely destroyed, until the mercury has been for some hours in contact with the gas.

To determine the volumetric changes, a thin capsule, filled with pure mercury and hermetically sealed, was placed in a vessel with a large reservoir of the usual form (fig. 1°), which was afterwards filled with dry oxygen. After the levels had been read, the silent discharge was passed until a considerable contraction was obtained. The corrections for changes of temperature and pressure were, as in other cases, furnished by an auxiliary vessel. The free end of the siphon tube having been sealed, the primary vessel was removed from the calorimeter, and the capsule broken by a sudden jerk. The breaking of the capsule, in this and other experiments, was greatly facilitated by introducing into the vessel a small piece of thick glass tube, which fell on the capsule when the vessel was shaken (fig. 1°, *k*, p. 347).

Viewing ozone as an allotropic form of oxygen, in the gaseous state, we expected that when mercury came into contact with it, a contraction would take place, equal to the volume of the ozone which entered into combination with the metal. This anticipation has not been realized. After the rupture of the capsule, the vessel was immediately replaced in the calorimeter and the levels read. Not the slightest diminution of volume was observed in any one of a large number of experiments; on the contrary, an increase, corresponding to a change of 1 millim. in the levels, generally occurred. On allowing the vessels to remain in the calorimeter, and reading the position of the acid in the siphon tubes from time to time, the gas was found to expand steadily, but slowly, for some hours, till from two-thirds to five-sixths of the contraction produced by the discharge was recovered. If the vessel was opened at any time while this expansion was going on, the ozone reactions were always manifest; but when the expansion was at an end, the ozone reactions had also ceased.

If the mercury, instead of being allowed tranquilly to act upon the gas, was violently agitated after breaking the capsule, a much smaller portion of the contraction was restored; in some cases not more than one-sixth.

Metallic *silver*, in the state both of leaf and of filings, gave similar results. The surface of the silver was partially blackened, about three-fourths of the original contraction was recovered, and the whole operation much more quickly terminated.

As the above reactions were evidently complex, the mercury and silver partly entering into combination with the gas, while the compounds formed appeared to exercise a catalytic action, we endeavoured to find an elementary body which would instantly destroy the ozone reactions, and at the same time be without action on dry oxygen. After some trials, we found that *iodine* possessed the required properties. We first ascertained that its vapour, although visible at common temperatures, has no appreciable tension. When a small capsule, containing pure and dry iodine, was broken in a vessel of the usual form filled with oxygen, the levels of the acid in the siphon tube were not altered. So slight also is the affinity of iodine for oxygen, that, on heating the reservoir so as to volatilize a considerable portion of the iodine, and afterwards allowing it to cool, the volume of the gas underwent no change. On the other hand, if ozone be present, the iodine is immediately attacked, a greyish-yellow compound is formed, and all ozone reactions are instantly destroyed.

The experiment already described with mercury was now repeated, substituting iodine for that metal. On breaking the capsule, the levels of the acid scarcely changed 1 millim., although the original contraction amounted to 50 millims. No subsequent expansion took place, and, on opening the vessel, the ozone reactions had entirely disappeared.

On the allotropic hypothesis, these experiments, and particularly the last, lead to the conclusion that ozone must have a density at least fifty times as great as that of oxygen. This conclusion is indeed unavoidable from the experiments just described, unless it is assumed that at the same moment when one portion of the ozone combines with the iodine, another portion changes back into oxygen, and that these quantities are so related to one another, that the expansion due to the one is exactly equal to the contraction arising from the other. Such a supposition cannot, however, be considered probable.

4. In order to subject this remarkable property of ozone to a further examination, two additional series of experiments were undertaken, to a description of which we now proceed.

In the first series, a primary and an auxiliary vessel with large reservoirs were filled with pure and dry oxygen, small capsules hermetically sealed, and containing portions of the same solution of iodide of potassium, having been previously placed in each. The silent discharge was passed through the primary vessel so as to produce a considerable contraction, amounting in different experiments to from 40 millims. to 80 millims. The levels of the acid in the siphon tubes of both vessels having been carefully read while the vessels were in the calorimeter, the ends were sealed, and the vessels shaken so as to break the capsules in both. In the primary vessel, the iodide of potassium solution became instantly coloured dark brown from the iodine set free, while that in the auxiliary vessel did not change. On replacing the vessels in the calorimeter, and opening the ends of the siphon tubes, the change in the levels indicated a considerable expansion in both. In the auxiliary vessel, this expansion was due to the tension of the vapour of the solution of iodide of potassium alone; in the primary vessel, the expansion ought to have been less than this, on account of the absorption of ozone, if the volume of that body were capable of measurement.

In the following Table, which contains the results of five very careful experiments made in this way, the first column gives the amount of contraction produced by the silent discharge in the primary vessel, previous to the breaking of the capsules; the second, the temperature; the third and fourth, the respective expansions in the primary and auxiliary vessels; and the fifth, the differences of the numbers in the third and fourth columns:—

	mm.	°	mm.	mm.	mm.
I.	81·5	11·0C.	68·5	70.0	—1·5
II.	62·2	13·5C.	79·5	80·0	—0·5
III.	72·2	8·7C.	50·7	52·0	—1·3
IV.	63·5	12·2C.	71·5	73·0	—1·5
V.	45·5	16·2C.	87·0	89·2	—2·2

The capacity of the vessels employed in these experiments was about 30 cub. cent., and the primary and its auxiliary were found, in each experiment, by careful comparative observations, to work accurately together. The solution of iodide of potassium was purposely employed of different strengths in the several experiments. In I. it contained $\frac{1}{400}$th part of iodide of potassium; in II. $\frac{1}{200}$th; in III. $\frac{1}{3}$rd; and in IV. and V. $\frac{1}{5}$th. In the two last the solution was slightly acidulated with hydrochloric acid, in the others it was neutral. The capsules contained each about 0·7 grm. of these solutions.

The agreement in the results of these experiments, made with solutions of iodide of potassium so widely differing, is very remarkable. We ought also to observe that direct experiments, performed with great care, showed that the iodine set free by the ozone in the primary vessel did not affect the tension of the vapour of the solution.

Taking the mean of the above numbers, the density of ozone, as compared with that of oxygen, must be expressed, on the allotropic hypothesis, by about the number 60; in other words, ozone must be a gas only about six times lighter than the metal lithium. If the small differences in the fifth column be due, wholly or in part, to accidental causes, which is far from improbable, a still higher number must, on the same hypothesis, be taken to express the density of ozone.

In the last series of experiments, the amount of iodine set free in the solution of iodide of potassium was determined by analysis, and the weight of oxygen deduced therefrom compared with the weight of oxygen, calculated from the volumetric change which had occurred in the formation of the ozone.

We shall describe these experiments with some detail, particularly as the methods employed will be found applicable to other cases of gas analysis, where small changes in a given volume of gas have to be estimated.

Before filling it with oxygen, a sealed capsule containing a solution of iodide of potassium was introduced into the primary vessel, while the auxiliary contained the dry gas only. The silent discharge was passed through the former, and the contraction carefully observed. The capsule was then broken, and the solution agitated in the primary vessel for a few seconds. The siphon tube was next cut off, and the liquid carefully washed out and analysed by means of a weak solution of sulphurous acid, the exact strength of which had been immediately before determined by observing the amount required to decolorize a solution containing a known weight of iodine.

In some of the experiments the solution of iodide of potassium was slightly acidulated, in the others it was neutral. In the latter case it was acidulated before being analysed. The results were the same, whether the solution was taken in the neutral or in the acid state. For although oxygen gas acts upon an acid solution of iodide of potassium, the action requires time, and the contact in this case was only continued for a few seconds.*

The formula by which we calculated the results of these experiments may be thus investigated:

Let f, g (fig. 1), be the mean level of the acid in the legs of the siphon tube; d, e, the levels at any time, t being the temperature, and Π the barometric pressure corrected for temperature. Let also $ge=fd=x$, and let H be the length of a tube similar to the siphon tube, and whose capacity is equal to that of the reservoir and of the siphon tube to f. Let a be the height of a barometer containing the liquid in the siphon tube, p the pressure of the gas in the vessel, and V the volume of the gas reduced to 0° C. and 760 millims.

Then evidently,

$$p \propto \mathrm{V}\frac{1+\alpha t}{\mathrm{H}+x}.$$

But

$$p=\Pi\left(1+\frac{2x}{a}\right),$$

hence

$$\frac{\mathrm{V}(1+\alpha t)}{\Pi(\mathrm{H}+x)\left(1+\frac{2x}{a}\right)}$$

is a constant quantity. Taking the logarithmic differential, we have

$$0=\frac{\delta \mathrm{V}}{\mathrm{V}}+\frac{\alpha\delta t}{1+\alpha t}-\frac{\delta\Pi}{\Pi}-\frac{\delta x}{\mathrm{H}+x}-\frac{\frac{2\delta x}{a}-\frac{2x\delta a}{a^2}}{1+\frac{2x}{a}}.$$

Now $\frac{\delta a}{a}=\frac{\delta\Pi}{\Pi}$ is multiplied by $\frac{x}{a}$, a quantity rarely exceeding $\frac{1}{200}$. To this degree of approximation, then, at least,

$$\frac{\delta \mathrm{V}}{\mathrm{V}}+\frac{\alpha\delta t}{1+\alpha t}-\frac{\delta\Pi}{\Pi}=\delta x\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right) \quad . \quad . \quad . \quad . \quad (1.)$$

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* BAUMERT has objected on this ground to some of the experiments in a former communication made by one of us to the Society. We have found that, in the circumstances in which those experiments were performed, about one-twentieth of the effect was due to this cause; but as the oxygen acting on the solution of iodide of potassium set free its equivalent of iodine, the equality of the numbers given in that paper could not be disturbed by this action. We have, since that time, by additional experiments, fully confirmed the statement that no water is produced in the destruction of electrolytic ozone by heat.

If $V_{,}$, $H_{,}$, $x_{,}$ represent for the auxiliary vessel the quantities corresponding to V, H, x in the primary, we have, since $\delta V_{,}=0$,

$$\frac{a\delta t}{1+at}-\frac{\delta\Pi}{\Pi}=\delta x_{,}\left(\frac{2}{a}+\frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \qquad (2.)$$

If $H_{,}=H$, *i. e.* if the primary and auxiliary vessels be of similar dimensions, we have at once, from (1.) and (2.),

$$\frac{\delta V}{V}=\delta x-\delta x_{,}\left(\frac{2}{a}+\frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.)$$

If the vessels be not similar, let

$$\delta x_{,}\left(\frac{2}{a}+\frac{1}{H_{,}}\right)=\delta x_{,,}\left(\frac{2}{a}=\frac{1}{H}\right),$$

then instead of (3.) we have

$$\frac{\delta V}{V}=(\delta x-\delta x_{,,})\left(\frac{2}{a}+\frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.)$$

Formula (3.) or (4.) gives the change of volume in the gas, as deduced from the observed change in the levels in the siphon tube.

For the estimation of the portion of the gas ($\delta_{,}V$) taken up as ozone by the solution of iodide of potassium, let C be the capacity of the primary vessel to f in litres, s the number of measures of sulphurous acid required to decolorize the solution when washed out of the vessel, S the number required to decolorize 1 grm. of iodine. Then we have, evidently, as a sufficient approximation,

$$\frac{\delta_{,}V}{V}=\frac{\dfrac{Is}{15{\cdot}8S}}{\dfrac{1{\cdot}4367Cp}{(1+at)760}}.$$

If we suppose ozone to be allotropic oxygen, with a relative density $e:1$, then $\delta_{,}V$ of oxygen contracts to $\frac{\delta_{,}V}{e}$ on being changed into ozone. Hence on this hypothesis,

$$\frac{\delta_{,}V}{\delta V}=\frac{e}{e-1}.$$

In order to verify this method, two similar vessels were filled with pure oxygen, one containing a capsule filled with a neutral solution of iodide of potassium, the other a capsule filled with an acidulated solution of the same salt, and of precisely the same strength. The neutral solution was also introduced into the siphon tubes of both vessels. After breaking the capsules, the levels were read, and the vessels set aside for some days; at the end of which time it was found that a portion of oxygen gas had been absorbed in the primary vessel which contained the acid solution, while no change had occurred in the other. The levels were now read again, and the solution in the primary vessel analyzed.

The weight of the oxygen absorbed, as calculated by the foregoing formulæ from the volumetric change, was 0·0002188 grm., while its weight deduced from the analysis was 0·0002181 grm. The close agreement between these numbers shows that the method is susceptible of considerable accuracy.

The following Table contains the results of six experiments made in the manner above described. The primary and auxiliary vessels were carefully constructed of similar dimensions, and were found, on trial, to work accurately together, so that formula (3.) was directly applicable.

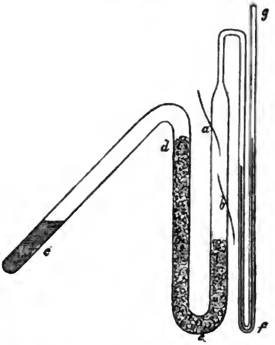
	I.	II.	III.	IV.	V.	VI.
	mm.	mm.	mm.	mm.	mm.	mm.
$2x_{,}$.	31·5	—3·0	—18·5	—48·5	—51·0	39·0
$2(x_{,}+\delta x_{,})$.	31·0	18·0	—2·25	—6·5	—9·75	—8·25
$2x$.	4·0	38·5	—0·5	16·5	72·5	65·0
$2(x+\delta x)$.	—78·0	—2·75	—55·25	—5·0	—39·0	—27·5
C.	0·0338	0·0306	0·0288	0·0279	0·0269	0·0346
s.	9·1	5·4	5·7	5·1	4·5	4·5
	grm.	grm.	grm.	grm.	grm.	grm.
I.	0·0268	0·0684	0·0442	0·0674	0·0446	0·0621
S.	22·6	47·95	30·85	49·5	36·8	44·43
	mm.	mm.	mm.	mm.	mm.	mm.
H.	777·0	772·5	763·0	751·0	747·2	751·0
t.	11°·0 C.	13°·45 C.	9°·1 C.	9°·8 C.	14°·0 C.	14°·7 C.
$\frac{1}{H}$.	0·000025	0·000024	0·000025	0·000026	0·000027	0·000036
$\frac{\delta_{,}V}{\delta V}$.	0·932	0·938	0·947	0·927	0·952	0·933

On comparing these experiments with the foregoing, it will be observed that they do not give exactly the same result. Interpreted as they stand, they indicate a density for ozone, if we may use the expression, more than infinite, inasmuch as the quantity of oxygen deduced from the analysis is less than' that corresponding to the contraction observed. But, although every precaution was taken to avoid all sources of uncertainty, it is not improbable that this difference between the amount of oxygen deduced from the contraction and from the analysis may arise from a slight defect in some of the data, particularly as it would only involve an error of the order of $\frac{1}{2000}$th of the entire gas.

Taking the mean result of the three series of experiments as they stand, it gives, on the allotropic hypothesis, almost exactly an infinite density for ozone.

5. The commonly received statement, that the whole of a given volume of dry oxygen gas can be converted into ozone by the passage of electrical sparks, is erroneous. In repeated trials, with tubes of different forms and sizes, we found that not more than one-twelfth of the oxygen could, under the most favourable circumstances, be converted into ozone, even by the silent discharge, and a much smaller proportion by the action of sparks. But if the ozone is removed as fast as it is produced, the conversion may be carried on indefinitely. An apparatus was constructed of the form shown in fig. 7. At *a*, *b* two fine platinum wires were hermetically sealed into the glass; at *c* there was a solution of iodide of potassium, and *de* was filled with fragments of fused chloride of calcium which allowed the ozone to pass freely, but arrested the vapour of the solution; so that while the discharge always took place in pure and dry oxygen, the ozone was gradually absorbed. The volumetric change was measured by the readings of the sulphuric acid in the siphon tube *fg* sealed at *g*. The experiment was continued till five-twelfths of the oxygen (whose entire volume was about 12 cub. cent.) was absorbed, and the action was still going on. It was not considered necessary to persevere further, as the labour of turning the machine was very great. To produce the effect just mentioned, the discharge from the machine in excellent order had to be passed through the tube for twenty-four hours.

Fig. 7.



When the electrical discharge is passed through rarefied oxygen, the phenomena are apparently the same as with the gas at the common pressure of the atmosphere. We filled a vessel with oxygen, and exhausted it till the pressure was equal to 1 inch of mercury, in the hope that in this rarefied state a larger portion of the oxygen might be converted into ozone than under greater pressures, but this did not prove to be the case. We intend on a future occasion to pursue this part of the inquiry, and to examine particularly the effects of the electrical discharge on oxygen in different states of rarefaction and condensation.

Ozone, obtained by electrolysis, gave results nearly similar to those already described. As the volume of the oxygen gas from which the ozone was derived could not, in the case of electrolytic ozone, be observed directly, it was estimated indirectly by placing three vessels in line, and passing the same stream of electrolytic oxygen through them all. By heating the first and last vessels to 300° C, and observing the expansion produced in each, it was easy to calculate the expansion which would have occurred in the middle vessel, if it had been exposed to similar treatment. This expansion was assumed to be equal to the contraction which occurs when ozone is produced from oxygen by means of the electrical discharge. Finally, the actual amount of ozone in the middle vessel was determined by introducing a solution of iodide of potassium, and ascertaining by analysis the amount of iodine set free. The individual experiments with electrolytic ozone did not agree so well with one another as those performed with ozone prepared by the discharge. This arose partly from the very small quantity of ozone in electrolytic oxygen, but chiefly from the irregularity in that quantity at different times, even when the current was passing very steadily, which made it difficult to ascertain with certainty the expansion due to the ozone in the middle vessel. Our earlier results, indeed, gave a measurable volume for ozone, and as a first approximation we obtained the number 4 as expressing its density.* But, by multiplying our experiments, and taking all possible precautions to ensure accuracy, we found that electrolytic ozone, like that produced by the discharge, has no appreciable volume.

Ozone is not condensed at common pressures by the cold produced by a mixture of solid carbonic acid and ether. A stream of electrolytic oxygen, passed very slowly, first through a U-tube surrounded by snow and salt, and next through a spiral tube immersed in the carbonic acid and ether bath (−76° C.), underwent no change. The ozone reactions, as the gas issued from the tube, after exposure to this low temperature, were as strong as before it entered the bath.

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* Proceedings of the Royal Society, vol. viii, p. 498, and vol. ix, p. 606.

6. *Hydrogen,* prepared with care by the action of dilute sulphuric acid recently boiled on zinc, and purified by passing through three U-tubes containing corrosive sublimate in solution, hydrate of potash, and sulphuric acid, respectively, and finally, in order to remove the last trace of oxygen, through a tube filled with metallic copper heated to redness, was found not to be altered in volume, either by the sparks or by the silent discharge. It appears to be a much better conductor of electricity than oxygen.

With *Nitrogen,* prepared in the usual way by depriving atmospheric air of its oxygen by means of heated copper, the results were also negative.

Among the compound gases, *Carbonic Acid* is rapidly decomposed by the spark, slowly by the silent discharge; in both cases expansion takes places.

Cyanogen is at once decomposed by the spark with deposition of carbon (?); but presents so great a resistance to the passage of electricity, that the action of the silent discharge could not be ascertained with certainty.

Protoxide of Nitrogen is readily attacked by the spark, with formation of hyponitric acid, whose characteristic red colour is distinctly seen. The primary result of the spark action is expansion, but on allowing the gas to stand, it gradually contracts, in consequence of the absorption of the hyponitric acid gas by the sulphuric acid in the siphon tube. It is impossible to determine the precise amount of the first expansion, as a certain amount of absorption occurs at the same time; but, in one imperfect trial, the ratio between the expansion and the subsequent contraction was nearly that of 1 : 2. This corresponds to the conversion of 8 vols. of protoxide of nitrogen into 4 vols. of hyponitric acid gas and 6 vols. of nitrogen. The silent discharge appears to produce the same result as the spark, but as the action is slower, the absorption interferes with any attempt to determine accurately the primary expansion.

Deutoxide of Nitrogen presents the interesting example of a compound gas, which, under the influence both of the spark and silent discharge, undergoes, like oxygen, a diminution of volume. This is independent of the subsequent absorption of the hyponitric acid formed. This gas is remarkable for the facility with which it is decomposed by both forms of discharge. The passage of sparks for two minutes, through a tube containing about 5 cub. cent., produced a contraction of the gas to nine-tenths of its original volume, followed after some time by a contraction not quite double of the former, from the absorption of the hyponitric acid gas. On continuing to pass sparks till the decomposition was finished, and waiting till the hyponitric acid gas was completely absorbed, the residue amounted to a little more than one-fourth of the original gas. This residue consisted of a mixture of 11 vols. nitrogen, and 1 vol. oxygen. It is evident that the final result is a little complicated, but there can be little doubt that the action of the spark is to convert 8 vols. of deutoxide of nitrogen into 4 vols. of hyponitric acid gas, and 2 vols. of nitrogen. This decomposition may be due to the immediate action of the discharge; or the deutoxide of nitrogen may, in the first instance, be resolved into equal volumes of nitrogen and oxygen, the latter combining as it is formed with undecomposed deutoxide.

Carbonic Oxide has given results of great interest, the investigation of which has already occupied a considerable time, although it is not yet completed. The principal facts have, however, been already ascertained, and as they present some remarkable analogies to those already described in the case of oxygen, we shall briefly allude to them here, reserving the complete investigation for a future communication.

The carbonic oxide was prepared by heating oxalic acid with an excess of sulphuric acid, and absorbing the carbonic acid by means of a strong solution of hydrate of potash. The gas, as it escaped from the end of the apparatus, did not produce the slightest turbidity in lime or baryta water, and was completely absorbed by an ammoniacal solution of the subchloride of copper.

On exposing this gas to the action of the silent discharge, a steady contraction took place, and the surface of the positive platina wire became covered with a continuous deposit of a bronze colour. After some time, a trace, but only a trace, of the same deposit appeared at the point of the negative wire. If, after a contraction of 50 millims. or 60 millims. of the siphon tube had been obtained, a few electrical sparks were passed through the gas, the greater part of the contraction was, as in the case of oxygen, destroyed. Heat acted in the same direction, but did not restore the gas altogether to its original volume.

On continuing to pass the silent discharge, the gas continued to contract, and the deposit to increase on the positive wire. Portions of the same deposit were also scattered about the sides of the tube, being probably thrown off from the same wire. The experiment was in some cases continued till the gas had contracted to about one-third of its original volume. To effect this contraction, the machine had to be worked for sixty hours. The residual gas consisted of carbonic acid, oxygen, and undecomposed carbonic oxide. A similar deposit was obtained when the discharge took place between gold instead of platinum wires. This deposit appeared to be soluble in water. Its quantity was so small that direct analysis was altogether impossible. Its composition may, however, be determined by fixing with precision the ratios of the volumes of the carbonic acid and oxygen produced. We have succeeded in devising a method by which this analysis may be effected even with less than 0·5 cub. cent. of the mixed gases, but this part of the investigation is still unfinished.

Atmospheric Air is the only gaseous mixture which we have exposed to the action of the silent discharge. Like pure oxygen, it undergoes a diminution of volume; but the operation is more quickly terminated and the contraction is less than with that gas alone. If, after the passage of the discharge, the vessel be set aside for some hours, the contraction will be found to augment; and if the gaseous mixture be now again exposed to the action of the discharge, a further contraction will take place. On the other hand, heat destroys a portion only of the contraction at first produced. All these facts are easily explained from the simultaneous formation of ozone and of one of the higher oxides of nitrogen, and the marked influence of the latter, when formed, in arresting the formation of the former. To the same cause we have succeeded in referring an apparently anomalous state of oxygen, produced by passing a stream of strong electrical sparks for some minutes, through that gas containing a trace of nitrogen. The oxygen becomes by this treatment incapable of contracting or of changing into ozone under the action of the silent discharge, and only recovers its usual condition by exposure to heat or by standing for some hours. If the nitrogen amounts to not more than $\frac{1}{300}$th of the entire volume, this condition cannot be produced more than two or three times. At first we supposed it to be a new (passive) state of oxygen, but we have now no hesitation in referring it to the presence of a trace of hyponitric acid gas produced by the electrical sparks.

7. It is perhaps premature to attempt a positive explanation of the facts now described regarding ozone. The foregoing investigation into its volumetric relations has, for the moment, rather increased than diminished the difficulty of determining the true nature of that body. To reconcile the experimental results with the view that ozone is oxygen in an allotropic form, it is necessary to assume that its density immensely exceeds that of any known gas or vapour; being, as we have seen, according to the first and second series of experiments (§§ 3 and 4), from fifty to sixty times that of oxygen, and according to the third series (§ 4) absolutely infinite. Even the former results would make it only six times less dense than the metal lithium, and would place it rather in the class of solid or liquid bodies than of gaseous. The question may then be fairly proposed,—Can this singular body, at common temperatures be actually a solid or liquid substance, whose particles, in an extremely fine state of subdivision, are suspended in the oxygen with which it is always mixed? This question will scarcely, we think, admit of an affirmative answer. Not only does

ozone, mixed as usual with oxygen, pass through several U-tubes containing fragments of pumice moistened with sulphuric acid, but it exhibits its characteristic reactions when left for many hours in tubes of this kind. Besides, there is not the slightest cloud visible in a tube filled with oxygen, even when one-twelfth of the gas has been converted into ozone, nor does any deposit appear after long standing.

Ozone may be formed under conditions which exclude the possibility of its containing, as a constituent, any element except oxygen, or the elements of oxygen, if that body should hereafter be shown to be compound. As has been before stated, our experiments may be reconciled with the allotropic view and an ordinary density, but still one greater than that of oxygen, if we assume that when ozone comes into contact with such substances as iodine, or solutions of iodide of potassium, one portion of it, retaining the gaseous form, is changed back into common oxygen, while the remainder enters into combination; and that these are so related to one another, that the expansion due to the former is exactly equal to the contraction arising from the latter. We do not, however, consider this supposition to be by any means probable, nor can it be easily reconciled with the results (§ 3) obtained when mercury acts on ozone.

If we consider the conditions under which ozone is formed, we shall find them to be different from those which produce allotropic modifications in other cases. Such elements, for example, as phosphorus or sulphur, are modified by the action of heat, and not by the electrical discharge. It is true, at the same time, that the destruction of ozone, or, on the allotropic view, its reconversion into oxygen, by exposure to a temperature of 270° C., is apparently analogous to that action of heat whereby common phosphorus is converted into the red variety.

Without rejecting the allotropic constitution of ozone, although the results of our volumetric experiments are certainly difficult to reconcile with it, it may not be uninstructive to consider whether the facts already known admit of a different explanation. As ozone is formed from pure and dry oxygen by the electrical discharge, if it is not an allotropic form of oxygen, the latter must be either a mechanical mixture of two or more gases, or it must be a compound gas. It is perhaps scarcely necessary to consider the former hypothesis, according to which, oxygen, in its ordinary state, would be a mechanical mixture, as atmospheric air is a mixture of nitrogen and oxygen. The contraction, which occurs when the electrical discharge is passed through oxygen, is at first sight indeed favourable to such a supposition, inasmuch as the combination of gases is usually accompanied either by a diminution, or no change of volume. But we have not been able to discover, in its other reactions, any facts which countenance this otherwise improbable view of the constitution of oxygen gas.

Finally, it remains to be considered, whether in the formation of ozone, oxygen does not undergo a more profound molecular change than is involved in an allotropic modification, whether, in short, this supposed element may not be actually decomposed. If, for the moment, we confine our attention to the phenomena which present themselves when the electrical discharge is passed through oxygen, this attractive hypothesis will be found to furnish a simple and plausible explanation of them all. It will be observed at once that the conditions under which ozone is formed from oxygen by the electrical discharge, are precisely those under which other gases, known to be compound, are decomposed. The electrical current is one of very high intensity, and therefore very favourable to decomposition: when passed in the form of the silent discharge, a large contraction takes place in the volume of the gas, which is partially destroyed by a few electrical sparks, and wholly by heat. With nitrogen and hydrogen no similar effects are observed, the volume of these gases being quite unaffected by either form of discharge.

The behaviour of carbonic oxide, when exposed to the action of the silent and spark discharge, corresponds remarkably to that of oxygen: the latter form of discharge, while producing itself only a limited contraction in carbonic oxide, destroying a part of the contraction produced by the former. Again when deutoxide of nitrogen is exposed to the action of the same agents, an immediate contraction takes place without any solid or liquid product being formed, showing that in certain cases of gaseous decompositions, the resulting gases occupy a smaller volume than the original compound.

If we assume that oxygen is resolved by the electrical discharge into a new compound (ozone), containing the same constituents as the oxygen itself, but in a different proportion, and into one of the constituents themselves, in the same manner as carbonic acid is resolved into carbonic oxide and oxygen, or nitric oxide into hyponitric acid and nitrogen, the results of our experiments will admit of an easy explanation. One of the simplest suppositions we can make for this purpose is, that two volumes of oxygen consist of one volume of U and one volume of V, united without condensation (U and V being the supposed constituents of oxygen), and that one volume of ozone consists of two volumes of U and one volume of V: and further, that by the action of heat, iodine, &c., ozone is resolved into U and oxygen.

The appearance of ozone at the positive pole in the electrolysis of water, and its formation by the agency of so active a body as ordinary phosphorus, do not seem unfavourable to its being the result of decomposition. But the same observation will not apply to its production by the action of acids on such bodies as the peroxide of barium. We certainly should not have expected to see a body derived from the decomposition of oxygen produced under the latter circumstances, and, although the facts connected with its production in these cases have not been studied with precision, yet there appears to be no doubt that ozone is actually formed.

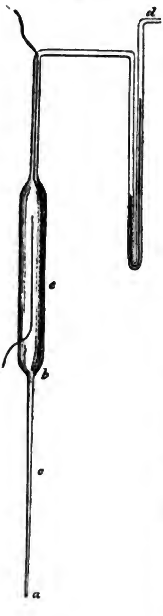
We must in conclusion add, that the few attempts we have made to isolate either of the supposed constituents of oxygen have failed.

We are still continuing to prosecute this inquiry, and hope on a future occasion to lay before the Society the results of further experiments which are now in progress.

Note, added July 12, 1860.

It having been suggested that a certain amount of the contraction produced by the passage of the electrical discharge through tubes containing oxygen might arise from the action on that gas of the platinum wires, or of finely divided platinum, which, as in Mr. Gassiot's experiment, might be thrown off by the action of the discharge, we have made the following experiment, in order to ascertain whether such an action could have occurred in the conditions under which we operated. Before describing the experiment, it may be proper to state, that in the passage of the discharge of the electrical machine, there is no visible separation of metallic platinum, as in that of the discharge from the induction coil, nor other evidence of the wires being acted on; on the contrary, both the wires and tube retain their original appearance after having been frequently exposed to the alternate action of the discharge and of heat.

Fig. 8.



A vessel, of the form represented in the annexed figure, was filled with pure and dry oxygen. It differs from the tubes usually employed only by having the lower end of the reservoir drawn out into a capillary tube *a b*. The platinum wires were inserted as usual, and an auxiliary vessel of the same size and form was filled with dry air. After determining the comparative range of the two vessels, their reservoirs were exposed, in the apparatus before described, to a temperature 300° C., in order to bring them as exactly as possible into the same condition. When they had cooled, the levels of the acid in the siphon tubes were again read, and the silent discharge was afterwards passed through the primary vessel till a contraction of twenty-seven millims. was obtained in its siphon tube. The extremity of the capillary tube of the reservoir was next cut off at *a*, and the end of the siphon tube *d*, which had the form represented in the figure, was dipped under sulphuric acid. The open end at *a*, was now connected with an apparatus, which supplied a slow stream of carefully dried air, and this was allowed to pass till the ozone and oxygen originally contained in the tube were entirely displaced by the dry air. It is obvious that by this arrangement the ozone was removed while the platinum wires and the inner surface of the tube were left in precisely the same state as after the passage of the discharge. The tube was next sealed off at *c*, by the application of the point of a fine blowpipe flame, the current having been arrested, so as to leave the usual column of sulphuric acid in the siphon tube. In sealing it, care was taken not to allow the air in *e* to become heated. The vessel was again placed, along with the auxiliary, in the calorimeter, and the levels read. The ends of the siphon tubes having been first sealed, the reservoirs were exposed to 300° C. An expansion should have taken place in the primary vessel, if the platinum had retained oxygen capable of being disengaged at 300° C,; but this was not found to be the case. The change of level in its sulphuric acid siphon(corrected by the auxiliary) did not amount to 0·2 millims., a degree of accuracy rarely attainable in these experiments.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 1st, 1860.

G. B. Buckton, Esq., in the Chair.

Rowlandson Cartmell, Esq., 81, High-street, Burton-on-Trent, was elected a Fellow of the Society.

Mr. H. C. Sorby laid before the meeting several specimens illustrating the artificial production of Pseudomorphs.

The following papers were read :—

"On the discrepancies in the statements of Pelouze and F. Mohr, respecting the solubility of Gallotannic acid in Ether," by Professor Bolley.

"On a hitherto unobserved source of Paraffin," by Professor Bolley.

The following donations were announced :—

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt in Wien," No. 4, for 1859: from the Institute.

"Jahrbuch der Central-Anstalt für Meteorologie und Erdmagnetismus in Wien," Band VI; from the Institute.

"Denkschriften der kaiserlichen Akademie der Wissenschaften in Wien," (math.-naturw. Classe), Band xviii.

"Sitzungsberichte derselben," Band xxxix, Hefte 1–5, und 1–12: from the Academy.

"Sitzungsberichte der königlich-baeyrischen Akademie der Wissenschaften," (math.-physikalische Classe) 1860, Hefte 1, 2: from the Academy.

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de Saint Pétersbourg," Tome 1, Feuilles 10–36: from the Academy.

"Memorie dell' Academia delle Scienze dell' Istituto di Bologna," Tomi 8, 9, e Parti I, del Tomo 10.

"Rendiconti dell' Academia delle Scienze dell' Istituto di Bologna, 1857–58, e 1858–59:" from the Academy.

"Boletin de la Societa de Naturalistas en Nueva Granada," 1860: from the Society.

"American Journal of Science and Arts," for May, July and September, 1860: from the Editors.

"Journal of the Franklin Institute," June to October, 1860: from the Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1860, Nos. 6–12: from the Academy.

"Proceedings of the American Philosophical Society," 1858, and January to June, 1859: from the Society.

"Smithsonian Report," for 1858: from the Smithsonian Institution.

"First Geological Report of Arkansas:" presented through the Smithsonian Institution, by the State of Arkansas.

"Canadian Journal," July to September, 1860: from the Canadian Institute.

"Memoirs of the Royal Astronomical Society," Vol. XXVIII.

"Monthly Notices of the Royal Astronomical Society," No. 9, for 1860: from the Society.

"Quarterly Journal of the Geological Society," No. 3, for 1860: from the Society.

"Chemical News," Nos. 29–44: from the Editor.

"Pharmaceutical Journal and Transactions," July to October 1860: from the Editor.

"Journal of the Society of Arts," Nos. 396 to 401, and 404 to 413: from the Society.

"Journal of the Photographic Society," July to October, 1860: from the Society.

"Literary Gazette," Nos. 105 to 121: from the Publishers.

"Proceedings of the Literary and Philosophical Society of Liverpool," 1859–60: from the Society.

"On the Lines of the Solar Spectrum," by Sir David Brewster, and Dr. J. H. Gladstone: from the Authors.

"On the Electric light of Mercury," by Dr. J. H. Gladstone: from the Author.

November 15th, 1860.

Professor Brodie, President, in the Chair.

The following Gentlemen were elected Fellows of the Society:—

J. H. Player, Esq., Oldbury, near Birmingham; A. Norman Tate, Esq., Runcorn Gap, near Warrington; Francis Valentine Paxton, Esq., B.A., Christchurch Oxford; George William Brown, Esq., 131, Sanchiehall-street, Glasgow; Henry Brunner, Esq., Royal Institution Laboratory, Manchester.

The following papers were read:—

"On the crystalline form of Metallic Chromium," by Professor Bolley.

"On the colouring matter of Persian Berries," by Professor Bolley.

"On the basic Carbonates of Copper," by Mr. F. Field.

Dr. Hofmann made a communication "On the Separation of the Volatile Ethyl-alkaloids."

The following donations were announced:—

"Om Sövandets Bestanddele og deres Förderling i Havet," by G. Forchhammer: from the Author.

"Recherches sur les Rapports reciproques des Poids atomiques," par J. S. Stass: from the Author.

"Du Raisin considéré comme Médicament," par J. C. Herpin: from the Author.

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de Saint Pétersbourg," Tome II, feuilles 1–17: from the Academy.

"Quarterly Journal of the Geological Society, No. 4," for 1860: from the Society.

"Elements of Chemistry," by William Allen Miller, Part II, "Inorganic Chemistry:" from the Author.

"On the Volumetric Relations of Ozone, and the action of the Electric Discharge on Oxygen and other Gases," by Thomas Andrews, and P. G. Tait: from the Authors.

"Chemical News," Nos. 46–49: from the Editor.

"Pharmaceutical Journal and Transactions," for November, 1860: from the Editor.

"Photographic Journal," for November, 1860: from the Photographic Society.

"Literary Gazette," Nos. 122, 123: from the Publishers.

"Notices of the Proceedings of the Meetings of the Members of the Royal Institution," 1859-60.

"List of Members, Officers, &c., of the Royal Institution," 1859.

"Additions to the Library of the Royal Institution," from July 1859, to July 1860: from the Royal Institution.

December 6th, 1860.

Col. Philip Yorke, Vice-President, in the Chair.

James Barratt, Esq., of Coniston, Windermere, Westmoreland, was elected a Fellow of the Society:—

A paper was read:

"On a new Lead-salt corresponding to Cobalt-yellow," by Mr. S. D. Hayes.

Dr. Hofmann made a communication "On the production of mixed Amines, Phosphines, and Arsines."

The following donations were announced:—

"Verhandlungen der naturforschenden Gesellschaft in Basel," 2th Theil, 4ter Heft: from the Society.

"Journal of the Franklin Institute," for November 1860: from the Institute.

"Journal of the Society of Arts," Nos. 414-419: from the Society.

"Pharmaceutical Journal and Transactions," for December, 1860: from the Society.

"Chemical News," Nos. 50-52: from the Editor.

"Literary Gazette," Nos. 125-127: from the Publishers.

"On the large Blasts at Holyhead," by George Robertson, Esq.: from the Author.

December 20th, 1860.

Professor **Brodie**, President, in the Chair.

The following were elected Fellows of the Society:—

Rev. W. R. **Bowditch**, Wakefield; **John L. W. Thudichum**, M.D., 65, South Audley Street.

The following papers were read:—

"Contributions to the Knowledge of the Laws of Gas-absorption," by **Thomas H. Sims**.

"On Sugar in Urine," by Dr. **H. Bence Jones**.

"On the Separation of Tellurium, Selenium and Sulphur," by Dr. **Oppenheim**.

"On Nitroprusside of Sodium," by Dr. **Oppenheim**.

The following donations were announced:—

"Abhandlungen der koniglich-baeyerischen Akademie der Wissenschaften (mathematisch-physikalische Classe)," Band VIII, Abtheilung 3.

"Sitzungsberichte derselben," 1860, Heft II.

"Denkrede an Alexander von Humboldt, gelesen in der öffentlichen Sitzung der königlich-baeyerischen Akademie der Wissenschaften," am 28 März, 1860, von C. F. P. von **Martius**:

from the Royal Bavarian Academy of Sciences.

"Öfversight af Kongl. Vetenskaps-Akademiens Förhandlingar, sextonde Årgången," 1859: from the Swedish Academy of Sciences.

"American Journal of Science and Art," for November, 1860: from the Editors.

"Monthly Notices of the Royal Astronomical Society, Vol. XXI, No. 1: from the Society.

"Chemical News," Nos. 52–54: from the Editor.

"Journal of the Society of Arts," Nos. 420, 421: from the Society.

"Photographic Journal," for December, 1860: from the Photographic Society.

"Literary Gazette," Nos. 128, 129: from the Publishers.

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THE

QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*Contributions to the knowledge of the Laws of Gas-absorption.*

By Thos. H. Sims,

(DALTON SCHOLAR IN THE LABORATORY OF OWEN'S COLLEGE, MANCHESTER).

It is well known that some gases, which at a given temperature obey, between certain limits, Boyle's law of pressure, have been found to deviate from the law when examined between the same limits of pressure, but at different temperatures. Thus Regnault* has shown that the volumes of carbonic acid gas measured, under different pressures less than that of the atmosphere, at the temperature of 0° C, do not vary inversely with the pressure; whereas measured between the same limits of pressure at 100° C., the deviation from Boyle's law becomes inappreciable. Considering these facts, it appeared not unlikely that the law known as Dalton and Henry's Law, according to which the weight of gas absorbed by a liquid at a given temperature under various pressures, is directly proportional to the pressure, would, upon investigation, show phenomena of a similar kind, so that the amount of deviation from the law of absorption which a given gas exhibits between certain limits of pressure may vary according to the temperature at which the absorption occurs. That many of the gases most soluble in water are not absorbed at the ordinary temperatures under different pressures in proportions even approaching those required by Dalton's law, has already been pointed out. Professor Roscoe† showed that chlorine gas, when mixed with varying amounts of both hydrogen and carbonic acid gas, is not absorbed in quantities proportional to the pressure; and Messrs. Roscoe and Dittmar* have recently proved that under directly measured pressures extending from 0·05 to 2 metres of mercury, both hydrochloric acid and ammoniacal gases are absorbed by water at 0° C., in quantities differing widely from those required by Dalton and Henry's law.

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* Regnault, Expériences pour déterminer, &c., p. 148.

† Chem. Soc. Qu. J., viii. 14.

Experiment has, up to the present time, left it undecided, whether this deviation from the law of absorption is solely dependent upon the chemical nature of the gases and liquids present, or, whether the relation between the amount of absorbed gas and pressure is at the same time influenced by change of temperature.

The object of the present research is to throw some light upon this question by determining the solubility of certain gases in water under considerable variation of direct pressure at different temperatures.

1.—*Sulphurous Acid in Water.*

The solubility of sulphurous acid gas in water, at various temperatures, and under the ordinary atmospheric pressure, has already been accurately determined by Schönfeld,† but no estimation of the quantity of gas absorbed under directly increased or diminished pressures has been made. Hence it appeared desirable to examine whether the conclusion drawn by Schönfeld from experiments made with mixed gases, viz., that at temperatures above 10° C., sulphurous acid obeys the law of absorption, was borne out by more extended observations of the solubility of the gas under directly measured pressures. For this purpose, a method of experimentation was adopted, similar in principle to that described by Messrs. Roscoe and Dittmar, in the memoir already mentioned, viz., determining by accurate analysis the quantity of gas absorbed by a known weight of water contained in a bulb-tube apparatus, under exactly specified conditions of temperature and pressure. The amount of the dissolved gas was estimated, according to the iodometric method, by carefully breaking the bulb under recently boiled water, diluting the solution to a given volume, and analysing an aliquot portion of the liquid again diluted with water, so that it contained only 0·05 p. c. of sulphurous acid. The strength of the standard iodine-solution was not determined in the usual way, by comparison with the iodine equivalent to the chlorine set free by hydrochloric acid, from a known weight of bichromate of potassium, but the volume of the standard solution was directly determined, which was required to oxidise completely a given weight of pure dry sulphurous acid, diluted with water to such an extent that the liquid contained only 0·05 p. c. of sulphurous acid. For this purpose, long-necked tubes, represented by Fig. 1, were blown before the blowpipe and accurately weighed; into these tubes was led a quantity of pure and dry sulphurous acid, which had previously been distilled and left no residue on evaporation. As soon as from 1 to 2 grms. of the liquid had collected in the tubes, they were hermetically sealed, and again weighed. When the determination was to be made, the neck of one of these tubes was opened under recently boiled water, whilst the bulb was placed in a freezing mixture, which was afterwards removed, so that the liquid acid began to distil over into the water. As soon as the acid had volatilised, and the water had been drawn back into the tube, the neck was cut off with a file, and both tubes washed well out with water. The solution of sulphurous acid was then diluted with boiled water up to 3,600 cb. c.; of this diluted solution, 100 cb. c. were taken for analysis, and the standard iodine solution was added drop by drop from a burette until the blue starch reaction became visible. From the quantity of solution thus required, and from the quantity of sulphurous acid employed, it was easy to find the weight of sulphurous acid corresponding to one cubic centimetre of iodine-solution. The following numbers give the weights of sulphurous acid oxidised by 1 cb. c. of the standard solution, as determined for solution No. I by four, and for solution No. II by six, separate experiments:

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* Chem. Soc. Qu. Jn., xii., 128.

† Ann. Ch. Pharm., xcv., 1.

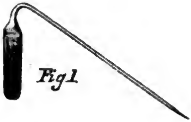

Fig 1

Solution No. I.		Solution No. II.	
Experiment 1 ..	0·001212	Experiment 1 ..	0·001200
„ 2 ..	0·001211	„ 2 ..	0·001208
„ 3 ..	0·001216	„ 3 ..	0·001204
„ 4 ..	0·001211	„ 4 ..	0·001210
		„ 5 ..	0·001200
Mean	0·001212	„ 6 ..	0·001210
		Mean	0·001205

In order to avoid the dangerous explosions which might ensue from the employment of flasks in which the gas is prepared from heated sulphuric acid and copper under a pressure of from two to three atmospheres, the liquefied acid was used as the source of gas. The supply of gas was obtained in a convenient form by evolving it in the usual manner from sulphuric acid and copper, and by well washing it through bulbs containing water, then passing it into glass tubes with long necks of about 15 cb-cs. capacity placed in a freezing mixture. As soon as the tubes were nearly filled with sulphurous acid, the necks were bent, as shown in Fig. 2, and afterwards closed before the blow-pipe. Each tube contained a sufficient quantity of sulphurous acid for one experiment, the tube *b* being of the same diameter as the neck of the bulb-apparatus to which it was directly attached.

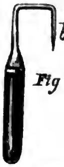

Fig 2

Different arrangements of the same method were adopted, according as the determination was to be made under a pressure, equal to, greater, or less than, the ordinary atmospheric pressure. For determining the absorption under ordinary pressures, one of the tubes of sulphurous acid was placed in a freezing mixture and opened by cutting off the narrow tube at *b*, Fig. 2, the end of this tube was then rounded before the blow-pipe, and connected by a carefully made double-sheet caoutchouc joining with the end *a* of a bulb apparatus, Fig. 3, of which the capacity and weight were known. The bulb *e* of this apparatus, capable of containing from 2 to 5 cb-cs. water, was placed in a water-bath, which was provided with arrangements for the supply of hot and cold, and for the egress of waste water. In this water-bath, and near to the bulb apparatus, was placed a thermometer which had been carefully compared with a normal instrument from the Kew Observatory. The temperature of the bath was easily kept constant at any required point, by continual agitation with a stirrer, and by running in, as required, hot or cold water. The apparatus was so arranged that the tube of liquid acid was fixed outside the water-bath, and at such a distance from it, that when operating at high temperatures, the heat might not cause too rapid an evolution of gas. In this way, a very steady stream of sulphurous acid could be passed through the bulb-tube without the slightest difficulty; the ordinary temperature of the atmosphere

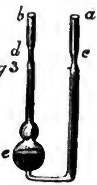

Fig 3

not being high enough to cause the gas to be given off too quickly, and the evaporation from the surface of the liquid acid cooling it down considerably. After the liquid in the bulb had been saturated, the gas was still allowed to pass through it for about 20 minutes longer in order to insure that the liquid attained the exact temperature of the water-bath. The limb of the bulb nearest to the tube of sulphurous acid was then closed by pressing the caoutchouc joining with a screw-clamp, and afterwards the other limb by pressing in a similar way a sheet-caoutchouc tube with which it was provided. The bulb was then separated from the tube of sulphurous acid, removed from the water-bath, placed in a freezing mixture and hermetically sealed at *c* and *d* (Fig. 3). The height of the barometer was then observed; the bulb and its contents, together with the ends of each limb, were again weighed; the temperature in the balance-case was noted; and also the height of the barometer at the time of weighing. The bulb was next carefully broken under water, and the solution diluted with water up to a certain known volume, such that the liquid did not contain more than 0·05 p.c. of sulphurous acid, the water in both cases having been recently boiled. An aliquot portion of this was then taken for analysis, and the amount of sulphurous acid it contained, was determined by the addition of starch and a standard iodine-solution, of which every cubic centimetre corresponded to a certain known weight of sulphurous acid.

From these data, the weight of sulphurous acid absorbed by one gramme of water at the observed pressure and temperature was easily calculated. An example will best show the mode of calculation. The following were the data obtained in one experiment :

Weight of bulb-apparatus empty = 21·0399 grms.
Capacity of apparatus to *c d*. = 18·38 cb.c.
Weight of bulb and contents = 24·3800 grms.
Barometer at closing = 746·9 mm.
Temperature of bath = 20° C.
Barometer at weighing bulb and contents = 748·2 mm.
Temperature in balance-case at weighing bulb and contents = 14° 5 C.
Tension of aqueous vapour at 20° C. = 17·4 mm.

The contents of the bulb diluted up to 1000 cb. c., of which 100 cb. c. required for oxidation 28·1 cb.c. of a standard iodine-solution, of which 1 cubic centimetre corresponded to 0·001212 grm. of sulphurous acid.

1000 cb. c. of sulphurous acid at 0° C. and 760 mms. weigh 2·8606 grms.

1000 cb. c. of air at 0° C. and 760 mm. weigh 1·294 grms.

From the above data we find that the total quantity of sulphurous acid would require 281 cb. c. of iodine solution. The whole of the sulphurous acid contained in the bulb weighed, therefore, $281 \times 0·001212 = 0·3406$ grm. The capacity of the bulb at 0° C. and 760 mms. was found to be 17·03 cb. c. The weight of this volume of air is 0·022 grm. The contents of the bulb, viz., the water and total sulphurous acid weighed $24·38 - 21.0399 = 3·3401$ grms. The weight of the contents and the weight of air displaced may therefore be taken as $3·3401 + 0·022 = 3·3621$ grms. This being taken as the capacity of the liquid in cubic centimetres, the volume of sulphurous acid gas contained in the bulb at 20° C., and under a pressure of $746·9 - 17·4 = 729·5$ mm. is $18·22 - 3·36 = 14·86$ cb. c. The weight of this gas was found to be 0·0382 grm. The sulphurous acid dissolved is, therefore, $0·3406 - 0·0382 = 0·3024$ grm. The weight of water which dissolves this weight of sulphurous acid is therefore $3·3621 - 0·3406 = 3·0215$ grms.

The weight of sulphurous acid which 1 grm. of water will dissolve at a temperature of 20° C. and a pressure of 729·5 mm. is therefore, $\frac{0·3024}{3·0215} = 0·1002$ grm. The volume of sulphurous acid measured at 0° C and 760 mms. which 1 grm. of water will dissolve, under the same circumstances, is found to be $\frac{105·7}{3·0215} = 35·0$ cb. c.

If the amount of gas absorbed were directly proportional to the pressure, at a temperature of 20° C., and under the normal pressure of 760 mm., 1 grm. of water would dissolve 0·1043 grm. and 1 cb. c. would dissolve 36·47 cb. c. of sulphurous acid.

Under pressures greater than that of the atmosphere, a bulb-apparatus similar to that used for ordinary pressures was employed. The requisite quantity of boiled water having been introduced into the bulb, a tube of liquid sulphurous acid *f* was attached by means of a sheet-caoutchouc joining to the limb *a* of the bulb (Fig. 4); to the other limb *b* was attached in a similar way, the burette-shaped apparatus C., which ,filled with mercury, is used for obtaining the necessary pressure. Between the tubes, thus connected with

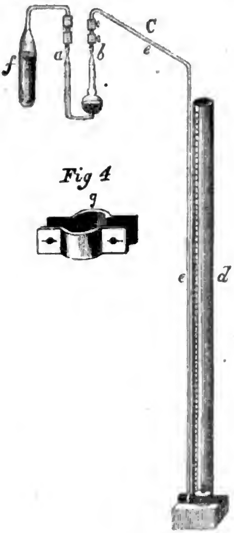
Fig 4

caoutchouc joinings, sufficient room was left, to allow them to be closed with screw-clamps at the conclusion of the experiment. To render these joinings able to withstand the pressure, they were first bound tightly to the respective tubes with copper wire, and over the middle portion of each of those joinings, a piece of brass foil was tightly folded which was allowed to overlap the glass tubes at both ends. Each of the ends of these pieces of foil was then tightly bound round with strips of sheet-lead, and these were secured to the tubes, by means of small iron semicircular screw-clamps (Fig. 4 *g*).

The apparatus thus put together was perfectly air-tight under pressures up to three atmospheres, and could be closed at pleasure, by pressing together the copper foil with screw-clamps. Into the wide tube *d* of the apparatus C, which was divided into millimetres, and was about 2000 mm. long, a small quantity of mercury was placed, so as to shut off all access of air to the other part of the apparatus. When the sulphurous acid evolved from the liquid acid in the tube *f*, and passing through the water in the bulb-apparatus, had expelled all the air from the apparatus, mercury was by degrees poured into the divided tube *d*, until the necessary pressure was reached; the joining nearest the tube of sulphurous acid was then closed, by means of a screw-clamp; the bulb-apparatus was placed in a freezing-mixture; and when the rise of the mercury in the tube *e* of the apparatus C, above that in the tube *d*, indicated a minus pressure in the bulb-apparatus, the sulphurous-acid tube was removed by sealing off the bulb-apparatus at the narrowed part of the limb *a*. The temperature of the freezing mixture was then gradually increased by pouring in water, until it became one or two degrees higher than the temperature at which the determination was to be made; the gas thus set free from the water in the bulb-apparatus, bubbled up through the mercury in tube *d*. When no more gas escaped, the bulb-apparatus was transferred to the water-bath, already described, in which it was kept at the required constant temperature; owing to the reduction of temperature the water in the bulb now dissolved a further quantity of gas, and in consequence, the mercury rose a small distance up the tube *e*. When the height of the column of mercury in this tube had remained constant for 20 or 30 minutes, the heights of both columns of mercury were read off on the scale upon the wider tube *d*. The second limb of the bulb-apparatus was then closed by pressing together the brass foil with a screw-clamp.

The bulb-apparatus was next removed from the water-bath, placed in a freezing mixture, and as soon as the tension of the liquid had become less than the pressure of the atmosphere, separated entirely from the rest of the apparatus by sealing it off at the narrowed part of the limb *b* (Fig. 4). The height of the barometer was then read off, the bulb and its contents weighed, the height of the barometer at weighing and the temperature of the balance-case being also noted. The contents of the bulb were then cooled down by placing it in a freezing mixture, and the amount of sulphurous acid was determined, as before described, by breaking it under recently boiled water, diluting the solution to a certain known volume, and taking an aliquot portion of this solution for iodometric analysis.

In order to determine the amount of the gas dissolved under pressures less than one atmosphere, the method was modified in the following manner. Instead of the bulb-apparatus (Fig. 3) employed in both the former cases, a simple bulb (Fig. 5) blown upon the end of a glass tube was made use of. These bulbs had a capacity of, from 10 to 30 cb.cs. Into one of such bulbs was introduced from 5 to 15 grms. of recently boiled water, which was then saturated with sulphurous acid, evolved from one of the tubes of liquid acid the water being kept just above 5° C., at which temperature the solid hydrate melts. As soon as the water in the bulb was saturated with sulphurous acid at this temperature, a sheet-caoutchouc tube containing a spiral of platinum wire, was bound with copper wire, on to the open end of the

Fig 5

bulb-tube. This bulb-tube was then connected in a similar way, by the other end of the caoutchouc tube, to the shorter limb of a syphon-shaped tube (Fig. 6), the longer limb of which was divided into millimetres and dipped under mercury contained in a glass trough. The syphon-shaped tube was previously filled with sulphurous acid gas.

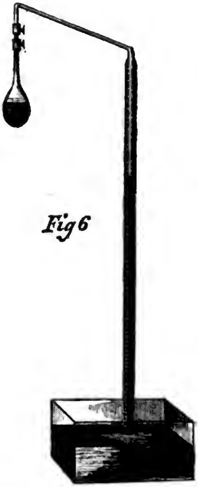
Fig 6

When the apparatus was thus arrranged, the liquid in the bulb was gradually heated; large quantities of sulphurous acid were thus evolved, and consequently the apparatus was soon freed from air. According as it was desired to have a greater or a less pressure, a smaller or larger amount of gas was expelled. The requisite amount of gas having been driven out, the bulb was placed in the water-bath, and kept constantly at the required temperature. Owing to the reduction of temperature of the water in the bulb, a portion of the gas in the bulb and tube was absorbed: consequently, the mercury rose in the divided tube. When the height of this column of mercury had remained stationary for about a quarter of an hour,—and the equilibrium was soon reached, if the liquid in the bulb was frequently agitated by shaking the bulb in the water-bath,—the height of the column of mercury was read off on the divided scale. The bulb was then closed, by pressing the caoutchouc joining with a screw-clamp, and removed from the rest of the apparatus by sealing it off at the narrowed part with the blow-pipe flame. The height of the barometer was then noted, the bulb weighed, and its contents analysed in exactly the same way as in the two former cases.

Determinations of the solubility of sulphurous acid in water under pressures varying between that of a few millimetres and that of three or four atmospheres, were made at each of four different temperatures, viz.: 7°C, 20°C, 39°·8C, and 50°C. The results of these experiments are arranged in the following Tables, in which P signifies the partial* pressure under which the absorption takes place; G signifies the weight, in grammes, of sulphurous acid which one gramme of water will dissolve under the partial pressure P; and V signifies the volume of gas, in cubic centimetres, which 1 grm. of water will dissolve under the partial pressure P.

For every temperature, two Tables are given. The direct experimental results are found in the first of each of these. Column II contains the weight of sulphurous acid absorbed by 1 grm. of water under the corresponding partial pressure arranged in Column I; Column III contains the weight of sulphurous acid which, according to each experiment, would have been absorbed under the standard pressure of 760 mm., upon the supposition that the amount of gas dissolved varies directly with the pressure. In Column IV is found the weight of sulphurous acid absorbed under the pressure P, calculated by means of a careful graphical interpolation from the numbers of Column II; and Column V contains the weight of sulphurous acid which, according to the graphical interpolation, would have been absorbed under a pressure of 760 mm., supposing that the gas obeyed Dalton and Henry's law. The second Table for each temperature contains a complete series of interpolated values for regular increments of pressure, seen in Column I; Column II gives the weight of sulphurous acid absorbed under the partial pressure P; Column III contains the weight of acid which, according to the values in the second column, would have been absorbed under the pressure of 760 mm., upon the supposition that the gas obeyed the law of absorption. The columns IV and V contain the volumes of sulphurous acid (measured at 0°C and 760 mm.), corresponding to the weights in Columns II and III respectively.

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* By partial pressure is meant, the total pressure under which the absorption takes place, minus the tension of aqueous vapour at the several temperatures.

Solubility of Sulphurous Acid in water at 7°C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
27·0	0·010	0·273	0·010	0·273
49·8	0·015	0·224	0·015	0·224
89·6	0·025	0·208	0·025	0·208
133·7	0·035	0·196	0·035	0·199
239·0	0·059	0·189	0·059	0·189
741·8	0·173	0·177	0·172	0·177
757·1	0·174	0·174	0·176	0·176
770·8	0·178	0·176	0·179	0·176
986·3	0·228	0·175	0·226	0·174
1291·0	0·293	0·172	0·293	0·172

Solubility of Sulphurous Acid in water at 7°C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760	V. at P.	V. at 760.
30	0·010	0·263	3·634	92·06	400	0·096	0·182	33·51	63·65
40	0·013	0·242	4·451	84·55	450	0·107	0·181	37·44	63·25
50	0·015	0·223	5·129	77·95	500	0·118	0·180	41·42	62·94
60	0·017	0·218	6·024	76·28	550	0·130	0·179	45·31	62·60
70	0·020	0·213	6·868	74·55	600	0·141	0·178	49·20	62·32
80	0·022	0·210	7·743	73·55	650	0·152	0·178	53·10	62·09
90	0·025	0·208	8·598	72·62	700	0·163	0·177	56·98	61·86
100	0·027	0·205	9·421	71·60	750	0·174	0·176	60·88	61.69
120	0·032	0·201	11·09	70·20	760	0·176	0·176	61·65	61·65
140	0·036	0·197	12·71	69·00	800	0·185	0·176	64·74	61·50
160	0·041	0·195	14·34	68·15	850	0·196	0·175	68·57	61·30
180	0·046	0·193	15·97	67·40	900	0·207	0·175	72·41	61·15
200	0·050	0·191	17·59	66·83	950	0·218	0·175	76·25	61·00
220	0·055	0·190	19·19	66·30	1000	0·229	0·174	80·01	60·88
240	0·059	0·188	20·79	65·84	1050	0·240	0·174	83·97	60·77
260	0·064	0·187	22·40	65·44	1100	0·251	0·174	87·80	60·65
280	0·069	0·186	23·99	65·10	1200	0·273	0·173	95·45	60·45
300	0·073	0·185	25·59	64·81	1300	0·295	0·172	103·00	60·25
350	0·085	0·184	29·55	64·16					

Solubility of Sulphurous Acid in water at 20° C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
32·4	0·006	0·148	0·006	0·148
50·1	0·009	0·138	0·009	0·138
65·0	0·011	0·133	0·011	0·133
77·3	0·013	0·127	0·013	0·129
78·4	0·013	0·129	0·013	0·129
82·2	0·014	0·126	0·014	0·126
121·8	0·020	0·113	0·019	0·121
291·0	0·043	0·111	0·043	0·117
446·6	0·064	0·109	0·064	0·108
658·2	0·094	0·108	0·091	0·105
728·9	0·100	0·104	0·100	0·104
729·5	0·100	0·104	0·100	0·104
730·8	0·100	0·104	0·100	0·104
1570·0	0·218	0·105	0·214	0·104
1911·0	0·260	0·104	0·260	0·104

Solubility of Sulphurous Acid in water at 20° C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760	V. at P.	V. at 760.
40	0·007	0·143	2·637	50·09	300	0·044	0·111	15·84	38·87
50	0·009	0·138	3·171	48·20	350	0·050	0·110	17·66	38·35
60	0·011	0·135	3·718	47·10	400	0·059	0·109	20·56	38·10
70	0·012	0·131	4·205	45·64	450	0·064	0·108	22·37	37·77
80	0·013	0·127	4·663	44·30	500	0·071	0·107	24·67	37·50
90	0·015	0·125	5·169	43·65	550	0·077	0·106	26·93	37·20
100	0·016	0·124	5·692	43·25	600	0·083	0·105	29·14	36·90
120	0·019	0·121	6·683	42·33	650	0·090	0·105	31·39	36·70
140	0·022	0·119	7·690	41·75	700	0·096	0·105	33·62	36·50
160	0·025	0·118	8·666	41·17	750	0·103	0·104	35·94	36·43
180	0·028	0·117	9·652	40·75	760	0·104	0·104	36·43	36·43
200	0·030	0·116	10·62	40·35	800	0·110	0·104	38·32	36·40
220	0·033	0·115	11·59	40·03	1000	0·137	0·104	47·85	36·37
240	0·036	0·114	12·54	39·70	1300	0·178	0·104	62·10	36·31
260	0·038	0·112	13·45	39·30	1600	0·218	0·104	76·35	36·27
280	0·041	0·112	14·41	39·10	1900	0·259	0·104	90·53	36·21

Solubility of Sulphurous Acid in water at 39·8° *C.*

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
205·9	0·017	0·062	0·017	0·062
293·1	0·023	0·060	0·023	0·061
696·0	0·054	0·059	0·054	0·059
697·6	0·054	0·059	0·054	0·059
701·6	0·053	0·055	0·053	0·059
1565·0	0·116	0·056	0·118	0·057
2021·0	0·150	0·056	0. 150	0·057

Solubility of Sulphurous Acid in water at 39·8° *C.*

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760.	V. at P.	V. at 760
200	0·016	0·062	5·675	21·57	760	0·059	0·059	20·50	20·50
300	0·024	0·061	8·368	21·20	800	0·062	0·059	21·58	20·50
400	0·031	0·060	11·03	20·95	1000	0·077	0·058	26·84	20·40
500	0·039	0·059	13·67	20·77	1500	0·113	0·057	39·65	20·09
600	0·047	0·059	16·29	20·64	2000	0·149	0·057	52·11	19·80

Solubility of Sulphurous Acid in water at 50° *C.*

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
191·5	0·011	0·011	0·045	0·045
664·0	0·039	0·039	0·045	0·045
1961·0	0·115	0·120	0·045	0·044

Solubility af Sulphurous Acid in water at 50° *C.*

II.

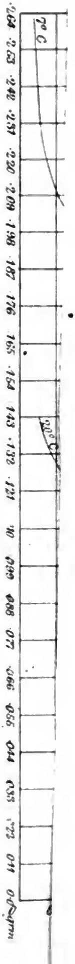
I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760	V. at P.	V. at 760.
200	0·012	0·045	4·156	15·79	800	0·047	0·045	16·43	15·60
400	0·024	0·045	8·275	15·72	1000	0·059	0·045	20·51	15·59
600	0·035	0·045	12·36	15·65	1500	0·088	0·044	30·73	15·57
760	0·045	0·045	15·62	15·62	2000	0·112	0·044	39·07	15·55

That at a temperature of 7° C., sulphurous acid is not absorbed by water in quantities directly proportional to the pressure is distinctly seen from the numbers in the third and fifth columns of the second Table for this temperature, which, instead of being equal to one another, or deviating on either side of a mean value, as they must do if Dalton's law of absorption were applicable, gradually decrease with increasing pressure. This variation from the law of absorption is also clearly seen by reference to the curve for this temperature (curve 7° Fig. 7) which graphically represents the relations expressed in Column III of the second Table, the pressures being arranged as abscissæ, and the numbers of Column III as ordinates.

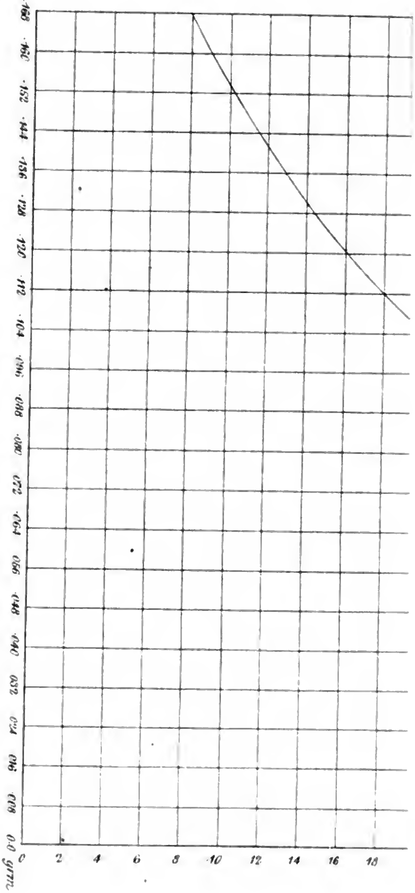
A similar examination of Columns III and V of the second of the Tables, giving the quantities of sulphurous acid absorbed at 20° C., as well as of the curve for this temperature (curve 20° Fig. 7) shows that at this higher temperature, also, the gas does not obey Dalton's law, and that the deviation, although smaller than at 7° C, is perfectly regular and perceptible. When the temperature at which the absorption occurs rises to 39°·8 C., the deviation from the law becomes still smaller, as is seen from the numbers in Columns III and V of the second Table for this temperature, as also from the corresponding curve (line 39°·8, Fig. 7) which closely approaches a straight line, parallel with the axis of x. At a temperature of 50° C, the quantity of sulphurous acid absorbed in water becomes directly proportional to the pressure, all variation between the several numbers in Columns III and V of the second Table, giving the experiments at this temperature, having become imperceptible. The same conclusion is arrived at by an examination of the horizontal straight line (line 50°. Fig. 7,) which gives a graphical representation of the same numbers.

From all these experiments we may therefore conclude, (I), that the deviations from the law of Dalton and Henry, which sulphurous acid and water exhibit, measured under pressures from 0·03 to 2 metres of mercury, vary according to the temperature at which the absorption occurs; and (II), that this deviation becomes less as the temperature increases, so that whilst below 40° C, the non-accordance with the law is considerable; above this temperature no variation can be perceived.

In the preceding Tables will be found the weight of gas dissolved by 1 grm. of water at each of the experimental temperatures, 7° C, SUL



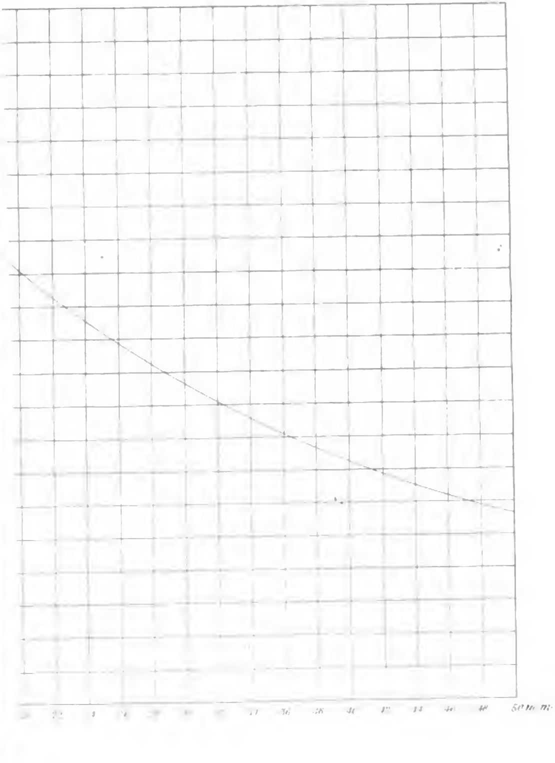
7° C
20° C
·264
·253
·242
·231
·220
·209
·198
·187
·176
·165
·154
·143
·132
·121
·110
·099
·088
·077
·066
·055
·044
·033
·022
·011
0·0 grm
6



·168
·160
·152
·144
·136
·128
·120
·112
·104
·096
·088
·080
·072
·064
·056
·048
·040
·032
·024
·016
·008
0·0 grm
0
2
4
6
8
10
12
14
16
18

PHUROUS ACID.

Fig VIII



20° C. 39°·8 C, 50° C, under a common partial pressure of 760 mm., reduced to this common pressure by interpolation of the direct observations at the several temperatures. From these values, those for the intermediate temperatures were obtained by graphical interpolation.

Column I of the following Table contains the temperatures; Column II contains the corresponding weights of sulphurous acid absorbed by 1 grm. of water; Column III contains the corresponding volumes of sulphurous acid absorbed by 1 grm. of water, all under a common partial pressure of 760 mm.

The line which represents the relation between the weight of sulphurous acid dissolved in water, under a pressure of 760 mm, and the temperature at which the absorption occurs may be seen by reference to Fig. 8.

Solubility of Sulphurous Acid in Water, at different Temperatures, under a pressure of 760 *mm. of Mercury.*

I.	II.	III.	I.	II.	III.
T°	G.	V.	T°.	G.	V.
8	0·168	58·7	30	0·078	27·3
10	0·154	53·9	32	0·073	25·7
12	0·142	49·6	34	0·069	24·3
14	0·130	45·6	36	0·065	22·8
16	0·121	42·2	38	0·062	21·6
18	0·112	39·3	40	0·058	20·4
20	0·104	36·4	42	0·055	19·3
22	0·098	34·2	44	0·053	18·4
24	0·092	32·3	46	0·050	17·4
26	0·087	30·5	48	0·047	16·4
28	0·083	28·9	50	0·045	15·6

The numbers in the above Table do not exactly agree with those formerly given by Schönfeld; the differences are, however, not more than can be easily accounted for by the employment of other methods, and by the fact that Schönfeld made his corrections for pressure dependent on Dalton and Henry's law, and that he neglected to subtract the tension of aqueous vapour from his barometric columns.

2. *Determination of the Tension of Sulphurous Acid.*

The method described, by which the absorption of sulphurous acid in water under pressures higher than the ordinary atmospheric pressure is estimated, led to the following simple method of determining the tension of the vapour of liquid sulphurous acid:—

One of the tubes of liquid sulphurous acid was hermetically sealed on to the tube *e* of the apparatus C (Fig. 4). The operation of sealing these tubes together is rather a difficult one, but when once done, the joining will bear with more rough treatment than one made of a caoutchouc tube covered with brass foil, and all possibility of escape or failure is avoided. The whole apparatus was first freed from air by allowing the sulphurous acid to pass for some time through a small quantity of mercury placed in the wider tube *d* of the apparatus C (Fig. 4); the tube *d* was then filled up with mercury. The tension of the sulphurous acid at any temperature was then determined by placing the tube of liquid acid in a water-bath of the required temperature, keeping it constant at the desired point, until the level of the mercury in the tube *e* was perfectly constant, and then reading off the height of the mercury in both tubes, and observing the barometric pressure.

The necessary corrections being made for reducing the column of mercury in the tube, and that in the barometer to 0° C., the tension of the gas was equal to the column of mercury in the tube + the height of the barometer.

The following Table shows the result of two series of such determinations, the tension of the gas at each temperature being given in millimetres. The tensions corresponding to those temperatures to which an asterisk is prefixed were obtained by direct experiment, the others by graphical interpolation from the experimental numbers.

Tension of Sulphurous-acid.

Temp. in °C	Tension.			Temp. in °C.	Tension.		
	I.	II.	III.		I.	II.	III.
*0°	1162·1	1162·2	1165·1	* 8°	1596·0		
1	1209·0			* 9	1655·4	1656·7	
2	1254·0			*10	1724·5	1720·3	1719·5
*3	1310·4	1309·7		*11	1790·8	1791·0	
4	1364·0			12	1862·0		
*5	1421·0	1421·3	1421·1	*13	1926·8	1930·1	
6	1473·0			14	2003·0		
*7	1531·4	1535·0		*15	2067·7	2072·3	2064·9

Since these experiments were made, Regnault has published* a series of determinations of the tension of the vapour of sulphurous acid. The close agreement of Regnault's numbers found in Column III of the above Table with the results of my own experiments in Columns I and II, may serve as a proof of the exactitude of the simple method which I have employed.

The results of the foregoing Tables are approximately given by the following formula, which was kindly furnished me by Prof. Clifton:—

$$\text{G at } 760 = \frac{2540}{t} - \frac{9205}{t^2} + \frac{100}{P}\left(\frac{10338}{t^2} - \frac{62760}{t^3}\right).$$

where G and P retain their former signification, and t represents the temperature in degrees centigrade.

The following Table shows the close agreement of the results calculated from this formula and those obtained by direct experiment:—

P	7°C.		20°C.		40°C.		50°C.	
	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
40·0	0·245	0·242	0·149	0·143				
50·0	0·231	0·223	0·140	0·138				
100·0	0·203	0·205	0·122	0·124				
200·0	0·189	0·191	0·113	0·116	0·061	0·062	0·049	0·045
500·0	0·181	0·180	0·108	0·107	0·059	0·059	0·049	0·045
800·0	0·175	0·176	0·108	0·104	0·058	0·059	0·048	0·045
1000·0	0·178	0·174	0·106	0·104	0·058	0·058	0·048	0·045
1200·0	0·177	0·173	0·105	0·104	0·058	0·057	0·048	0·045
1800·0			0·105	0·104	0·058	0·057	0·048	0·044
2000·0			0·105	0·104	0·058	0·057	0·048	0·044

3. *Ammonia in Water.*

The experiments made by Professor Roscoe and Mr. Dittmar, on the absorption of ammonia† in water prove that, at the temperature of 0°C., this gas does not obey Dalton and Henry's law of pressures. Since all their experiments with this gas, under various pressures, were made at a temperature of 0°C. (those made at higher temperatures being all under the ordinary atmospheric pressure), I was induced to extend the enquiry to pressure experiments at higher temperatures, in order to determine whether ammonia, like sulphurous acid, was dissolved at higher temperatures more nearly in accordance with Dalton's law of absorption.

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* Comptes Rendus, tome, l. p. 1063. 11 Juin, 1869.

† Chem. Soc. Qu. J., vol. xii, p. 128.

The temperatures which were selected for experiment were 20°C., 40°C., and 100°C. Before commencing these determinations, I made several experiments at 0°C.; but, finding that my results corresponded sufficiently with those obtained by Messrs. Roscoe and Dittmar, I was satisfied to take their numbers as expressing the solubility of ammonia under various pressures at 0°C. The experiments made with ammonia were conducted in a way exactly similar to that employed for the sulphurous acid, at least under pressures equal to, and less than that of the atmosphere. As source of ammonia gas, a mixture of about equal weights of chloride of ammonium and slacked lime was used, the gas, before entering the absorption-bulbs, being well washed by passing through a series of bulbs containing water. In the experiments made under pressures greater than that of the atmosphere, the water in the bulb-apparatus, after being attached to the tube *e* of the apparatus C (fig. 4), was saturated with ammonia at a temperature of about 20°C.; the limb next the flask in which the ammonia gas was generating was then sealed off, the other limb still remaining connected with the tube *e* of the apparatus C by a sheet-caoutchouc joining covered with brass-foil. The bulb and contents were then gradually heated up to the temperature at which the determination was to be made, the necessary quantity of mercury, according to the pressure required, being introduced into the wider tube *d* of the apparatus *c* (fig. 4.) When the bulb had remained in the bath at the required temperature for some length of time, and the height of the mercury in the tube *e* remained constant, the bulb was closed in the usual way, and the ammonia contained in it was determined by analysis in the following manner:—The bulb, after being weighed, was broken in a beaker-glass under water containing a known volume of a standard hydrochloric acid solution, the strength of which had been accurately determined, according to Gay Lussac's well-known volumetric method, with pure silver. Care was taken to have more hydrochloric acid present than was necessary to neutralise the ammonia in the bulb, the excess of acid being determined by the addition, from a burette, of a standard soda solution, until the litmus was rendered blue.

The following Table contains the direct results of experiments made under various pressures at each of the temperatures 0° C., 20° C, 40° C, 100° C. P signifies the partial pressure on the gas in millimetres; and G signifies the weight in grammes of ammonia absorbed at the various temperatures by one gramme of water under the pressure P. Column III in this Table, for each temperature, contains the weight in grammes of ammonia which one gramme of water will dissolve, reduced from the numbers found in Column II, to a common pressure of 760 mm., on the supposition that the gas is dissolved in quantities directly proportional to the pressure. For the temperature 0°C., the results in the Table, marked with an asterisk, were taken from Messrs, Roscoe and Dittmar's paper, in order to complete the series at 0°C. The results at the other pressures agreeing so nearly with those of these chemists, that it was not considered necessary to make a complete series of determinations at this temperature.

Solubility of Ammonia in Water.

I.

P.	0° C.		P.	20° C.	
	G at P.	G at 760.		G at P.	G at 760.
I.	II.	III.	I.	II.	III.
20·7	0·084	3·101	45·5	0·100	1·666
*97·0	0·274	2·147	206·1	0.236	0·871
*241·0	0·463	1·460	735·4	0·508	0·525
*452·0	0·652	1·096	1525·0	0·811	0·404
749·6	0·888	0·900	2076·0	1·018	0·373
757·7	0·900	0·903			
*1963·0	2·137	0·827			

P.	40° C.		P.	100° C.	
	G at P.	G at 760.		G at P.	G at 760.
I.	II.	III.	I.	II.	III.
75·8	0·050	0·497	688·4	0·067	0·074
184·3	0·112	0·461	1078·0	0·104	0·073
701·1	0·322	0·349	1419·0	0·135	0·073
1599·0	0·522	0·248			
2129·0	0·599	0·214			

The following Table contains a series of interpolated values for the several temperatures, which were obtained by measurement, from the graphic representations of the direct observations, made at each of the temperatures 0° C., 20° C., 40° C., and 100° C., which are contained in the preceding Table.

Solubility of Ammonia in Water.

II.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
P.	0°C.		20°C.		40°C.		100°C.	
	G. at P.	G. at 760.	G. at P.	G. at 760.	G. at P.	G. at 760.	G. at P.	G. at 760.
20	0·082	3·113						
30	0·117	2·960						
40	0·148	2·820						
60	0·199	2·522	0·119	1·513				
80	0·240	2·280	0·141	1·337	0·052	0·497		
100	0·280	2·127	0·158	1·200	0·064	0·490		
120	0·316	2·000	0·173	1·095	0·076	0·483		
140	0·346	1·880	0·187	1·017	0·088	0·476		
160	0·375	1·780	0·202	0·962	0·099	0·470		
180	0·398	1·684	0·217	0·918	0·109	0·462		
200	0·421	1·598	0·232	0·881	0·120	0·455		
250	0·472	1·434	0·266	0·810	0·145	0·440		
300	0·519	1·315	0·296	0·750	0·168	0·426		
350	0·563	1·223	0·325	0·705	0·191	0·414		
400	0·606	1·152	0·353	0·670	0·211	0·402		
450	0·650	1·100	0·378	0·638	0·232	0·392		
500	0·692	1·052	0·403	0·612	0·251	0·382		
550	0·732	6·012	0·425	0·587	0·269	0·372		
600	0·770	0·975	0·447	0·566	0·287	0·363		
650	0·809	0·946	0·470	0·550	0·304	0·355		
700	0·850	0·923	0·492	0·534	0·320	0·347	0·068	0·074
750	0·891	0·903	0·514	0·521	0·335	0·339	0·073	0·074
760	0·899	0·899	0·518	0·518	0·338	0·338	0·074	0·074
800	0·937	0·888	0·535	0·508	0·349	0·332	0·078	0·074
850	0·980	0·876	0·556	0·497	0·363	0·325	0·083	0·074
900	1·029	0·869	0·574	0·485	0·378	0·319	0·088	0·074
950	1·077	0·862	0·594	0·475	0·391	0·313	0·092	0·073
1000	1·126	0·855	0·613	0·466	0·404	0·307	0·096	0·073
1050	1·177	0·852	0·632	0·457	0·414	0·300	0·101	0·073
1100	1·230	0·850	0·651	0·450	0·425	0·294	0·106	0·073
1150	1·283	0·848	0·669	0·442	0·434	0·287	0·110	0·073
1200	1·336	0·846	0·685	0·433	0·445	0·282	0·115	0·073
1250	1·388	0·844	0·704	0·428	0·454	0·276	0·120	0·073
1300	1·442	0·843	0·722	0·422	0·463	0·271	0·125	0·073
1350	1·496	0·842	0·741	0·417	0·472	0·266	0·130	0·073
1400	1·549	0·841	0·761	0·413	0·479	0·260	0·135	0·073
1450	1·603	0·840	0·780	0·409	0·486	0·255		
1500	1·656	0·839	0·801	0·406	0·493	0·250		
1600	1·758	0·835	0·842	0·400	0·511	0·242		
1700	1·861	0·832	0·881	0·394	0·530	0·237		
1800	1·966	0·830	0·919	0·388	0·547	0·231		
1900	2·070	0·828	0·955	0·382	0·565	0·226		
2000			0·992	0·377	0·579	0·220		
2100					0·594	0·215		

From the graphical representations of the values at the several temperatures, the experiments for each temperature were reduced to a common pressure of 760 mm. These values will be found in the preceding Table: from them the numbers contained in Column II of the following Table, which are the weights in grammes of ammonia absorbed by one gramme of water under a pressure of 760 mm., at the several temperatures in Column I, were obtained by graphical interpolation.

Solubility of Ammonia in Water at different temperatures, under a pressure of 760 *mm, of Mercury.*

I.	II.	I.	II.
0° C	0·899	52° C	0·274
2 ,,	0·853	54 ,,	0·265
4 ,,	0·809	56 ,,	0·256
6 ,,	0·765	58 ,,	0·247
8 ,,	0·724	60 ,,	0·238
10 ,,	0·684	62 ,,	0·229
12 ,,	0·646	64 ,,	0·220
14 ,,	0·611	66 ,,	0·211
16 ,,	0·578	68 ,,	0·202
18 ,,	0·546	70 ,,	0·194
20 ,,	0·518	72 ,,	0·186
22 ,,	0·490	74 ,,	0·178
24 ,,	0·467	76 ,,	0·170
26 ,,	0·446	78 ,,	0·162
28 ,,	0·426	80 ,,	0·154
30 ,,	0·408	82 ,,	0·146
32 ,,	0·393	84 ,,	0·138
34 ,,	0·378	86 ,,	0·130
36 ,,	0·363	88 ,,	0·122
38 ,,	0·350	90 ,,	0·114
40 ,,	0·338	92 ,,	0·106
42 ,,	0·326	94 ,,	0·098
44 ,,	0·315	96 ,,	0·090
46 ,,	0·304	98 ,,	0·082
48 ,,	0·294	100 ,,	0·074
50 ,,	0·284		

By a comparison of the Tables of the absorption of sulphurous acid in water with those of ammonia, it is evident that at low temperatures neither of these gases is absorbed directly as the pressure: for the observed amounts dissolved, under low pressures, at low temperatures, are much larger than the calculated amounts reduced from the observed amounts dissolved under ordinary pressures, at the same temperatures, to the several low pressures at which determinations were made, on the supposition that the gases obeyed Dalton and Henry's law.

From the preceding Tables it may also be seen that both gases, as the temperature increases, become gradually absorbed in quantities more nearly directly proportional to the pressure. At a temperature of 50° C, sulphurous acid appears to be absorbed quite in accordance with the law; whilst ammonia appears to obey the law at 100° C. A graphical representation of the pressure experiments made upon ammonia at different temperatures will be found on reference to Fig. 9.

The lines in Fig. 9, it must be noticed, represent the relation between the pressures and the numbers obtained by reducing the observed volumes of gas dissolved under the several pressures to a common pressure of 760 mm., on the supposition that the gas obeyed Dalton and Henry's law. Fig. 10 gives the line which represents the relation between the temperature, and the weight of ammonia absorbed, under a pressure of 760 mm.. by one gramme of water.

II.—*On Sugar in the Urine.*

By H. Bence Jones, M.D., F.R.S.

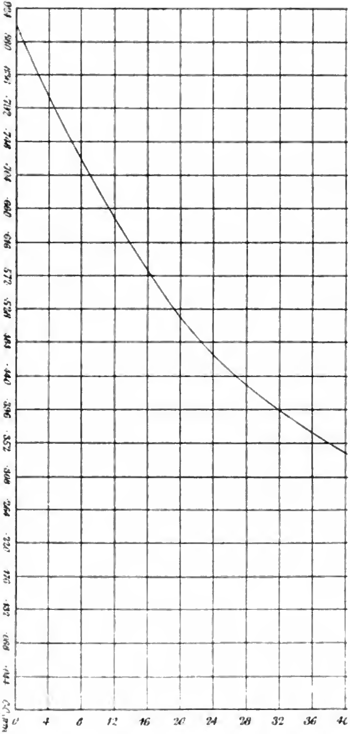
Part 1. *On the detection of Sugar when added to Healthy Urine.*

The detection of small quantities of sugar in water and in a solution containing organic and inorganic substances, constitute two questions as different as the detection of small quantities of arsenic or opium when dissolved in pure water or in a compound fluid.

Nothing is easier than to determine the presence of small quantities of sugar, arsenic, or opium in distilled water; but when organic matters are also present, the difficulty of the analysis becomes sometimes excessive. Very small quantities cannot be detected. The limit that can be found varies with each substance, according to the nature and amount of the organic matter present, according to the process of separation used, and according to the skill of the chemist.

In cases of poisoning, the separation of the poison from the contents of the stomach, or from the substance of the different

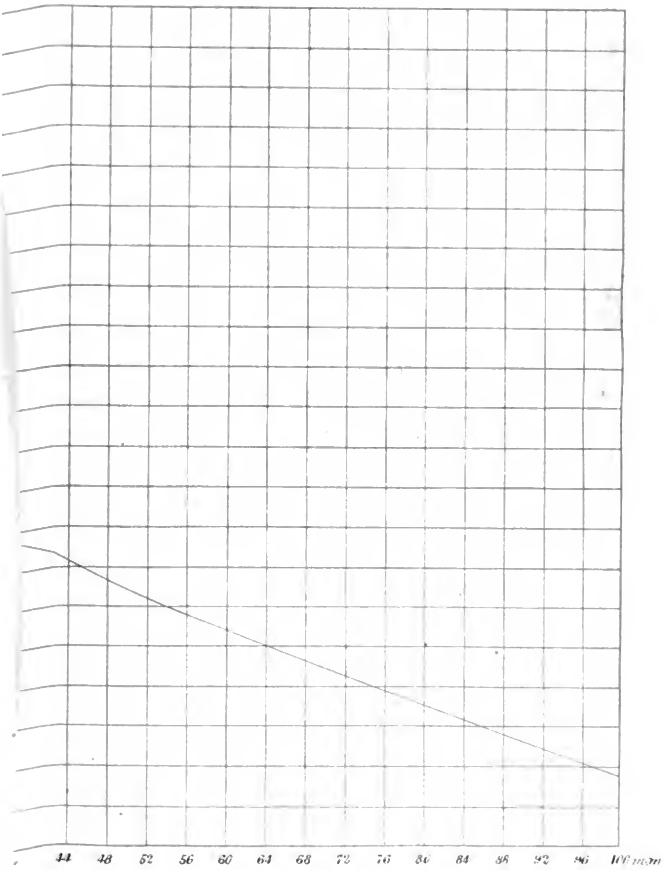
3·36
3·22
3·08
2·94
2·80
2·66
2·52
2·38
2·24
2·10
1·96
1·82
1·68
1·54
1·40
1·26
1·12
·98
·84
·70
·56
·42
·28
·14
0
mm.
0° C.



·924
·880
·836
·792
·748
·704
·660
·616
·572
·528
·484
·440
·396
·352
·308
·264
·220
·176
·132
·088
·044
CC. mm.
0
4
8
12
16
20
24
28
32
36
40

MMONIA.

Fig. X.



organs of the body, constitutes the whole difficulty; and this is also true regarding the detection of sugar. Whatever process is used for separating the sugar and the organic matter, some difficulties will be met with, and some limit to the quantity of sugar that can be detected will be found.

It is the object of the first part of this paper to show the difficulties and limits which exist when Lehmann's process for detecting sugar in the urine, or the fermentation process, or Soleil's Saccharimeter, or Brücke's processes are used.

I am much indebted to Drs. Ulrich and Valentine for carrying out my wishes, and for making the results as trustworthy as possible.

Lehmann's Process.

In his "Physiological Chemistry" (Translation, p. 285, vol. i), Lehmann says, "If a specimen of urine contain very little sugar, it is advisable to extract the solid residue with alcohol, to precipitate the sugar by the alcoholic solution of potassa, to dissolve the compound of sugar and potassa in water, and then to apply the sulphate of copper test."

Some experiments were first made on the solubility of potass-sugar in alcohol of different strengths.

200 c. c. of alcohol were made of three different degrees of strength, 90°, 80°, 70°, and the same amount of grape-sugar was added to each. The rotation was found, by the saccharimeter, to be between 8° and 9°; the temperature was 18 C. (64° F.) The sugar was precipitated by potassa, washed with absolute alcohol, and dissolved in water; and the solutions were neutralised with hydrochloric acid, evaporated, decolorised, and examined by the saccharimeter. The alcohol of 90° then gave 4° of rotation. The alcohol of 80° gave 2° of rotation. The alcohol of 70° gave no rotation.

A similar experiment was repeated with an amount of sugar which gave 11° to 12° rotation. The alcohol of 90° gave 6° of rotation. The alcohol of 80° gave 4½°.

1 grn. of pure grape-sugar was dissolved in 50 c. c., in 100 c. c., and in 150 c. c., of an alcohol between 80° and 90°, and potassa dissolved in alcohol of the same strength was added to each solution. In each a precipitate fell, but, after standing many hours, it was scarcely perceptible at the bottom of each glass.

1 grn. of sugar in 300 c. c. of alcohol between 80° and 90°, gave a scarcely perceptible precipitate with potass-alcohol.

On the other hand, the whole of the sugar was precipitated when 6 grns. of sugar were dissolved in 200 c. c. of methylated alcohol of 99°; and when 3 grns. were dissolved in 150 c. c. of alcohol of 98° to 100° treated with potassa, and the sugar-potassa determined by the saccharimeter, the whole was regained.

These experiments show that the evaporation of the urine must be carried nearly to dryness in order that the residue may be treated with nearly absolute alcohol. It was therefore necessary to determine the effect of the evaporation on the sugar added to the urine. Known quantities of sugar were added to urine before and after evaporation.

1000 c. c. of urine were evaporated; 6 grns. of sugar were then added to the residue, which was extracted with alcohol 98°, and ultimately 3 grns. of sugar were recovered.

325 c. c. of urine, treated the same way with 8 grns. of sugar gave 5½ grns. A second experiment gave the same result.

If to 100 c. c. of urine 8 grns. of sugar were added, and the evaporation in the water-bath was carried to dryness; 5 grns. were recovered by extraction with alcohol.

A second experiment gave the same result.

When the same quantity of sugar was added to 500 c. c., 4 grns. were recovered.

If to 500 c. c. urine 15 grns. were added, between 7 and 8 were recovered after evaporation.

In 1000 c. c., when 8 grns. of sugar were added, only 2 grns. were recovered. When the same quantity was added to 2000 c. c., a trace only was detectable.

Hence, during evaporation of small quantities of urine, there is but little decomposition of the sugar that is added; but when large quantities of urine are evaporated in the water-bath, much sugar is lost; and Lehmann's process for detecting small quantities of sugar in the urine is not sufficiently delicate.

On the Fermentation Test.

Of all the tests for sugar, the most conclusive, when it can be obtained, is the production of carbonic acid and alcohol by yeast.

The following points were examined:—1. Whether equal quantities of yeast give off equal quantities of carbonic acid,—that is, whether any error arises from deducting the quantity of carbonic acid given off by the yeast itself from the quantity given off by the yeast and sugar together? 2. What is the least quantity of sugar in water and urine that can be detected? 3. What effect urea, oxalate of urea, and the residue of the urine have on the process of fermentation? 4. What is the delicacy of the test as compared with the saccharimeter and Fehling's solution?

1. On the carbonic acid given off by yeast washed once with water:—

324·28 grns. of yeast gave 1·57 carbonic acid = 0·42 grns. per cent.
421·50 „ „ 1·79 „ = 0·48 „

In second experiment,—

240·70 grns. of yeast gave 0·75 carbonic acid = 0·31 per cent.
321·47 „ „ 1·00 „ = 0·31 „

2. What is the least quantity of sugar in water and urine that can be determined?

Half a grn. of grape-sugar with 29·99 grns. yeast, gave 0·39 grn. carbonic acid.

33·08 grns. yeast without any sugar being added gave 0·16 grn. carbonic acid.

Therefore 29·99 grns. yeast gave 0·14 grn. carbonic acid.

Hence, half a grn. of sugar gave 0·39 − 0·145 grn. carbonic acid = 0·24.

Theoretically = 0·24.

In a second experiment, after the yeast had been well washed to remove every trace of alcohol, the following numbers were obtained:—

Half a grn. of sugar, with 40·58 grns. of yeast, gave 0·34 carbonic acid.

Without sugar, 52·27 grns. of yeast gave 0·06 ∴ 40·58, give ·046.

Hence, half a grn. of sugar gave 0·34 − 0·05 = 0·29 carbonic acid.

The residue, after fermentation, was put into the smallest possible retort, and heated to boiling. The first drops that came over were tested for alcohol thus:—To one cubic centimetre of a moderately strong solution of bichromate of potassa, two or three drops of concentrated sulphuric acid were added, and then a few drops of the liquid supposed to contain alcohol. Heat was then gently used, and the fluid immediately became green from the alcohol present.

Hence, half a grn. of sugar in water gives carbonic acid that can be weighed and alcohol that can be detected.

One grn. of sugar was then added to 6 cubic centimetres of urine, and this fluid, without concentration, was fermented, and the sugar was detected. But if 1 grn. of sugar was added to 50 c. c. of urine, and this evaporated to 5 or 6 c. c., no fermentation occurred on the addition of yeast; neither was any fermentation observed when two or three grains of sugar were added.

If 3 grns. of sugar were added to 30 c. c. of urine, and this evaporated to 20 c. c,, the fluid quickly fermented, and the loss of weight was nearly the theoretical quantity.

The effect of urea and of oxalate of urea* was then determined.

The same sugar-solution was fermented without urea and with a small quantity of urea.

	Without Urea.		With Urea.
	1st Exp.	2nd Exp.	
Apparatus with sugar solution and yeast	1493·10	1506·63	1402·60
„ without „ „ „	1340·30	1351·60	1286·48
Yeast	152·80	155·03	116·12
Apparatus before fermentation . .	1493·10	1606·63	1402·60
„ after „ „	1472·26	1485·73	1381·64
Carbonic acid given off	20·84	20·90	20·96

Hence, the presence of the urea did not affect the fermentation.

If a concentrated solution of urea was taken, and 3 grns. of sugar were added to 6 c. c. of solution, no trace of fermentation occurred.

When 4 grns. of oxalate of urea were added to 34·6 grns. of sugar in solution, fermentation proceeded; but if much oxalate of urea was present, fermentation was stopped.

	4 grns. of Oxalate of Urea.	Much oxalate.
Apparatus with oxalate of urea and yeast	1618·90	1416·23
„ without „ „ „ .	1400·62	1295·08
Yeast	218·28	121·15
Apparatus before fermentation . .	1618·90	1416·23
„ after „ . .	1603·76	1415·20
Carbonic acid given off	14·94	1·03
Carbonic acid given off by yeast alone .		1·00

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* Experiments were made with oxalate of urea, because this substance existed in the fermenting fluid when the urea was chiefly removed by oxalic acid added to the concentrated urine.

Hence, with much oxalate, the fermentation was almost entirely stopped.

On the comparison of the delicacy of the Fermentation-test, and with Fehling's standard solution.

A watery solution of grape sugar was prepared which gave a solution of 104°=2·288 grains of sugar in each cubic centimetre.* 15 c. c. of this solution=34·25 grains of sugar were fermented with yeast that had been once washed. A second experiment was made with the same quantities, and a third experiment was made to determine the carbonic acid in the yeast:—

	1st Experiment.	2nd Experiment.	3rd Experiment.
Yeast employed .	263·90	270·66	210·15
Carbonic acid given off	18·29	18·70	0·62
Carbonic acid in yeast	0·76	0·78	
Carbonic acid in sugar	17·53	17·92	
Hence sugar in each c.c. of solution	=2·376 grains	=2·437 grains	

10 c. c. of the same solution were diluted to 160 c.c., and tested by fresh prepared Fehling's solution.

10 c. c. of Fehling's solution were reduced by 5·6 c. c. of the diluted sugar solution.

Hence 10 c. c. of the solution before dilution contained 21·9 grains sugar, and each c. c. contains 2·192 grains sugar.

Hence in each cubic centimeter of the solution there were present:—

By fermentation, 2·371 and 2·437 grs. sugar mean	=2·356 grs.
By saccharimeter	2·288 grs.
By copper test	2·192 grs.

On Soleil's Saccharimeter.

Before the saccharimeter can be used, the fluid about to be examined must be decolorised. To effect this, animal charcoal, acetate or subacetate of lead and ammonia, or chlorine gas must be used. These substances, whilst removing the colour, keep back or destroy some of the sugar, and it was desirable therefore to determine the loss.

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* This number is obtained by making a solution of sugar which contains .01 gramme of sugar in each cubic centimetre when examined by Fehling's solution. This amount of sugar in solution gives seven degrees of rotation.

First, charcoal:—A colourless solution of sugar which gave 7° of rotation was mixed with animal charcoal, boiled for a few minutes, and left for a few minutes longer, before it was filtered. The charcoal was washed three or four times with hot water. The washings were added to the fluid which first came through, and the whole was then found to give the same rotation as at first.

A fluid, dark brown from the colouring matter of the urine had three grains of sugar added to it, and it was then mixed with animal charcoal; after standing some time, it was filtered, and as it was not colourless, it was again treated with animal charcoal, and this was repeated a third time. The animal charcoal was many times washed with hot water. The clear fluid ultimately obtained was examined by the saccharimeter, and the loss was found to be not more than the frequent filtrations might account for.

A colourless solution of sugar in water gave between 9 and 10° of rotation. 75 c. c. of this solution were shaken with a small quantity of purified and fresh-burnt animal-charcoal, the fluid was then filtered, and the charcoal was not washed. The solution then gave between 7° and 8° of rotation.

75 c. c. of the same solution with twice the quantity of animal charcoal gave a rotation between 5° and 6°.

75 c. c. of the same solution with three times the quantity of animal charcoal, gave a rotation of between 4° and 5°.

One volume and a half of the same sugar-solution was mixed with one volume of animal charcoal. The clear fluid which passed through the filter was found to have lost half its rotating power.

It follows from these experiments, that a large excess of animal charcoal retains much sugar, and that the more charcoal used the less sugar passes through the filter; but all the sugar that is kept back can be washed out with boiling water.

It was desirable to know how much charcoal could be used without perceptible loss of sugar. 50 c. c. of a pure solution of sugar gave 27° of rotation. It was mixed with between 55 and 60 grains of charcoal shaken and filtered, and then gave 26°.

25 c.c. of a nearly colourless diabetic urine were diluted to 55 c.c.; the rotation was then between 15° and 16°. 50 c. c. of the same urine, shaken with 60 grs of charcoal, gave a colourless solution which rotated between 31° and 32°.

Some experiments were made with wood-charcoal to see its effects on sugar and on the colouring matter of the urine.

The wood-charcoal was finely powdered, but not fresh burnt.

One volume of pure sugar solution was shaken with half a volume of wood charcoal, and left to stand for some time. The solution gave 19° of rotation both before and after treatment. The same charcoal was shaken with urine, the fluid which filtered through was nearly as dark coloured as at first.

These experiments were repeated with fresh burnt wood charcoal. The solution of sugar was not affected. The colouring matter of the urine was partly removed, but the whole of the colour could not thus be taken away.

On the action of basic and neutral acetate of lead on solutions of sugar.

Dr. E. Robiquet, in his instructions for using his diabetometer, says that 25 c. c. of diabetic urine are to be mixed with 1 c. c. of extract of lead and 1 c. c. of liquid ammonia. The whole is to be shaken for some minutes to give a deposit. If the clear liquid is not completely decolorised, the same quantity of lead and ammonia is again to be added. If the decoloration is then complete, the amount of sugar may be determined by the amount of rotation observed.

25 c. c. of sugar-solution were diluted to 50 c. c. with water. Two experiments gave 21° and 22° of rotation. The same quantity of the same solution was mixed with 20 c. c. of neutral acetate of lead and 2 c. c. of ammonia, and the whole was diluted to 50 c. c. after filtration the rotation was found to be, in the first experiment, between 18° and 19°, and in the second experiment 18°. 25 c. c. of sugar-solution diluted to 50 c. c. gave between 9° and 10° of rotation. 25 c. c. of same solution with 2 c. c. of acetate of lead and 2 c. c. of liquid ammonia, and the whole diluted to 50 c. c. gave only 7° of rotation.

By using three times as much solution of lead and ammonia, the rotation was only 4° to 5°.

On the action of basic acetate of lead alone.

50 c. c. of urine were mixed with a solution of sugar which gave 9° of rotation; after precipitation by basic acetate of lead it was found to have lost 3° of rotation. A second experiment gave the same result.

A urine which gave between 8° and 9° of rotation gave from 5° to 6° after precipitation. The lead-precipitate was washed with hot water on the filter and boiled with hot water, but the sugar could not be removed.

In order to compare the action of basic and neutral acetate of lead on saccharine urine and on solutions of sugar in water alone, and in water with common salt and water and phosphate of soda, the following experiments were made.

A pure sugar-solution gave 10° to 11° of rotation; when mixed with common salt and precipitated by basic acetate of lead, it gave the same rotation; when more common salt was used, no difference was observed.

A solution of sugar which gave 9° of rotation was mixed with solution of common salt and urate of soda, and precipitated by basic acetate of lead; the rotation was then found to be between 7° and 8°. When the quantity of salt and urate of soda was less, the rotation was 8°.

A solution of sugar giving between 10° and 11° of rotation was mixed with much phosphate of soda, and then precipitated by basic acetate of lead: it then gave 8° to 9°.

A solution of sugar which gave 5°, after being mixed with much phosphate of soda and precipitated by basic acetate of lead, gave from 3° to 4° of rotation.

A solution giving 10° to 11°, mixed with a little urate of soda, and then precipitated by basic acetate of lead, gave 10° of rotation.

When neutral acetate of lead was used instead of basic acetate, very different results were obtained.

A pure sugar-solution gave 10° to 11° of rotation. When the solution was mixed with common salt, phosphate, and urate of soda, it gave, after precipitation, 10° to 11° of rotation, and the rotation was unchanged when a greater amount of these salts was added before precipitation.

1st. These experiments confirm the fact that a pure solution of sugar is not precipitated either by basic or by neutral acetate of lead, but that sugar is precipitated by neutral acetate of lead and ammonia.

2nd. Basic acetate of lead when added to saccharine urine causes the precipitation of some sugar. The urates and phosphates in the urine cause this precipitation of sugar, and not the chloride of sodium; for when a solution of sugar in water is mixed with chloride of sodium, basic acetate of lead causes no precipitation of the sugar. But when urate or phosphate of soda also is present, then some sugar is precipitated.

3rd. When neutral acetate of lead is added to solutions of sugar containing chloride of sodium, phosphate, and urate of soda, no precipitate of sugar occurs.

On the action of Chlorine.

Into a solution of sugar in water containing 6 grains of sugar to 20 c.c. of water, chlorine gas free from hydrochloric acid was passed for half an hour. It was left for twenty-four hours, and then hardly any difference of rotation was observed.

Into a solution of the same strength, chlorine was passed for an hour and a half, and it then was left for twenty-four hours; the loss was less than a grain of sugar.

325 c. c. of urine were mixed with 3 grains of sugar and to 20 c. c. The concentrated fluid was heated for twenty minutes with chlorine. It had then a yellowish urine colour, which could not be removed by further exposure to chlorine, and the subsequent use of animal charcoal did not give a solution which could be examined by the saccharimeter.

Pettenkofer's Test.

The fluid in which sugar is suspected is decolorised as far as possible, and then mixed with a few drops of a concentrated solution of glychocholic acid in soda or cholalic acid. Three or four drops of concentrated sulphuric acid are then added, and the whole gently heated without boiling. If sugar is present, a purple colour is seen at the edge of the watch glass: this is more evident on a white ground.

A standard solution of grape-sugar was made, 1 c. c. containing 0·005 sugar, and 5 drops of the solution = 1 milligramme, and was mixed with cholic acid and concentrated sulphuric acid: intense purple blue immediately formed.

One drop of this solution = 0·0002 of sugar, mixed with cholic and sulphuric acid gave, after a few minutes, a slight purple red and ultimately a tinge of blue.

5 drops of diabetic urine containing 7 grs. of sugar to the ounce of urine were mixed with cholic acid, and a strong sulphuric acid. After a few minutes, a slight purple red appeared which ultimately became bluish.

One drop of this diabetic urine without decoloration gave a purple red. Cholalic acid was found to have the same reaction as cholic acid.

Trommer's Test.

Among the different ways of employing this test, that recommended by Lehmann was found to be best. By it, $\frac{1}{20}$ per cent. (or 0·24 gr. to 1 oz.) of sugar added to the urine was easily detected by deposit of suboxide of copper.

2 or 3 c. c. of urine are mixed with a few drops of potassa and filtered, and then an equal quantity of strong potassa is added, with about 3 drops of a solution of sulphate of copper; the whole is well shaken, and the clear liquid poured off from the hydrated oxide of copper which has not dissolved. If the blue solution when heated (long boiling is quite unnecessary) becomes colourless without depositing suboxide of copper, then two drops more of the sulphate of copper should be added, and the experiment repeated. A separation of suboxide is often thus obtained, provided the boiling has not been continued so long at the first heating as to decompose the sugar.

Pure grape-sugar in water gives the well-known red suboxide. In urine, the suboxide is bright yellow or dirty yellow. When 0·01 gramme of grape-sugar dissolved in water was precipitated by acetate of lead and ammonia, and the precipitate treated with a little oxalic acid solution, the sugar solution gave a dirty yellowish reduction with standard copper-solution.

A solution of grape-sugar was mixed in different proportions with a solution of chloride of ammonium. The separation of the suboxide of copper was stopped, when the solution containing $\frac{1}{200}$ of a grain of sugar also contained 1 grain of chloride of ammonium. In some experiments, the suboxide of copper was deposited whilst ammonia in quantity was being given off.

The same series of experiments were made with urea and grape-sugar: the urea hindered the separation of the suboxide, when a solution containing $\frac{4}{1000}$ of a grain of sugar contained also 1 grain of urea.

Brücke's Processes.

Professor Brücke has published two processes for detecting small quantities of sugar in urine.

In the first or alcohol process, he advises that the urine should be mixed with four times its bulk of absolute alcohol. An alcoholic solution of potassa is then to be added, and the fluid is left for twelve hours to deposit potassa-sugar. The alcohol is then to be poured off, and the deposited matter dissolved in water and tested by reduction and other tests.

According to the experiments described in the early part of this paper, when small quantities of sugar exist in solution, an alcohol of 80 per cent. will only give from one-third to a scarcely perceptible quantity of the sugar which existed in a solution. If a very small quantity of sugar was present, this percentage of alcohol would therefore fail to detect it. With absolute alcohol by this process, the whole of the sugar is precipitated, but if the percentage of alcohol falls below 80, little or no sugar will be obtained. An alcohol of 90 per cent. gives only half the sugar that is present; and hence this method of Professor Brücke is very imperfect and very costly; even with methylated spirit.

In his second process, he recommends that the urine should be precipitated with neutral acetate of lead and then with basic acetate of lead, and after filtering off the precipitate, ammonia should be added; in this last precipitate the chief part of the sugar present will be found. What is the amount of sugar which, when added to the urine, can be detected by this process?

145 c. c. of fresh morning urine were treated with acetate of lead, basic acetate of lead, and then ammonia. 5 c. c. of a standard solution of sugar containing 0·025 gramme = $\frac{1}{3}$ of a grain nearly of sugar, was added before precipitation. The solution was almost free from colouring matter after precipitation by basic acetate of lead and quite free when precipitated by ammonia.

On adding 20 drops of a standard solution of copper to the potass solution of the subacetate of lead, no red suboxide of copper formed, but a dirty suboxide of copper fell. The solution of the ammonia precipitate in oxalic acid gave only a trace of red oxide, but plenty of dirty coloured suboxide. In the cold after 24 hours the same reduction occurred.

200 c. c. of fresh morning urine were treated as in the last experiment, but only 0·012 gramme = $\frac{1}{6}$ of a grain of sugar was added. The oxalic acid solution of the ammonia precipitate gave with 10 drops of copper solution a slight reduction, a dirty yellowish precipitate was obtained on boiling. The potash solution of the subacetate of lead precipitate destroyed the blue colour of the sulphate of copper solution but gave no precipitate.

200 c. c. of fresh mid-day urine were treated as before, 0·05 gramme = $\frac{3}{4}$ of a grain of sugar was added. The three precipitates were examined as well as the solution filtered from the ammonia precipitate.

1. The acetate of lead precipitate gave no reduction.

2. The basic acetate of lead precipitate was dissolved in potassa and gave no reduction; the blue colour of the copper solution disappeared however.

3. The precipitate with ammonia was treated with solution of oxalic acid, and on the addition of 4 c. c. of standard-copper solution a good reduction was obtained of a yellowish colour.

4. The clear liquid from the ammonia precipitate gave no reaction of sugar.

200 c. c. of fresh urine were treated as before; only ·01 gramme = $\frac{1}{7}$ of grain of sugar was added. The oxalic acid solution contained as usual the whole of the sugar. 2 c. c. of copper solution gave a dirty yellowish precipitate.

When the same quantity of grape-sugar was added to distilled water and treated in the same way, the oxalic-acid solution tested by the standard copper solution gave the same dirty-yellow precipitate.

To 700 c. c. of urine a known quantity of solution of grape-sugar giving 12° of rotation of the saccharimeter was added. The urine was treated as before. The ammonia precipitate decomposed by oxalic acid, contained sufficient sugar when diluted to the known quantity to give a rotation of 8°. Instead of decomposing the ammonia precipitate by oxalic acid, sulphuretted hydrogen was used, and if requisite this was twice repeated; the filtrate is then almost colourless, even when 5000 c. c. of urine have been used for an experiment.

To 1300 c. c. of urine a known quantity of a solution of grape sugar was added, giving 13° of rotation. In the ammoniacal precipitate enough sugar was found to give between 7° and 8° of rotation.

To 1137 c. c. of urine a known quantity of sugar solution was added, giving 11° to 12° of rotation in the ammoniacal precipitate; enough sugar was found to give, with the same quantity of water, 8° to 9° of rotation. This experiment when repeated gave in the ammoniacal precipitate 8° of rotation.

Hence by Brücke's lead process, when $\frac{3}{4}$, $\frac{1}{3}$, $\frac{1}{6}$, $\frac{1}{7}$ of a grain of grape-sugar are added to about 200 c. c. of urine, decided evidence of sugar was found in the ammonia precipitate. And by the quantitative experiments it appears that about two-thirds of all the sugar added can be recovered by this process.

The results of these experiments on the detection of sugar when added to the urine may be thus summed up:

1. Lehmann's process for detecting sugar in the urine cannot be employed when small quantities of sugar are present in large quantities of urine; by evaporation and decoloration, all the sugar is lost.

2. The process of fermentation is stopped by the residue of the urine, by much urea and by oxalate of urea still more decidedly. Half a grain of sugar in water can be detected by the alcohol produced, and may be determined approximatively by the carbonic acid given off; but in concentrated urine much larger quantities will be entirely overlooked.

3. In decolorising the urine for use in the saccharimeter, sugar is always lost; animal charcoal retains sugar in proportion to the amount of charcoal used. When the urine is decolorised by basic acetate of lead and ammonia, two-thirds of the sugar may be lost.

4. Pettenkofer's test for sugar is the most delicate test known; $\frac{2}{3}$ of a milligramme in distilled water, can be detected by it, and a little colouring matter of the urine does not hinder the reaction. If much colouring matter is present, it must be removed.

5. Trommer's test is capable of discovering $\frac{1}{20}$ per cent. of sugar in the urine, but when very small quantities of sugar are in solution with hydrochlorate of ammonia or urea, the reduction of the oxide of copper is not perceived; $\frac{1}{200}$ of a grain of sugar with 1 grain of hydrochlorate of ammonia, in water, gives no reduction; and $\frac{4}{1000}$ of a grain of sugar with 1 grain of urea stopped reduction.

6. Brücke's processes.

In the alcohol process if 80 per cent. alcohol is used, only $\frac{1}{4}$ or less of the sugar is obtained: and even by 90 per cent. alcohol one-half is lost. The necessity for so much absolute alcohol as will give with the urine a mixture of 90 per cent., makes the process nearly useless.

By Brücke's lead process, the best results have been obtained; $\frac{1}{7}$ of a grain of sugar in 200 c. c. of urine could be detected, and $\frac{2}{3}$ of all the sugar added was recovered. Moreover, when sulphuretted hydrogen is used to decompose the ammonia precipitate, the sugar is obtained in a state fit for fermentation, and free from colour, so that the saccharimeter can be employed.

PART 2.—*On the detection of sugar naturally present in healthy urine.*

The presence or absence of sugar in healthy urine is not only of great interest in relation to the true comprehension of the nature of diabetes, but it is also of importance in respect to our knowledge of the chemical changes which occur in the body in health.

If sugar exists in the urine in health, as Brücke maintains, then diabetes must be considered as an exaggeration of a healthy state, and not as a distinct and peculiar condition of the system; and it will be necessary to admit, that in health and in diabetes, the same chemical changes take place in the system, but that the greater amount of change in the one case constitutes health, and the lesser amount in the other case is called diabetes.

Professor Brücke deserves all credit for the accuracy of his observations, and for the clearness of his statements; and though I failed by the alcohol process to satisfy myself of the truth of the results which he obtained by that method, yet, by his lead process, I have fully convinced myself, after a lengthened investigation, which only the perseverance of Dr. Ulrich could have carried out, that there is sugar in healthy urine; and that, in addition to the proofs of its presence mentioned by Professor Brücke, it may be detected and measured by the saccharimeter; and that by fermentation, alcohol in recognisable quantity may be obtained.

On the detection of sugar in healthy urine, by Brücke's alcohol process.

140 c. c. and 200 c. c. of fresh urine were mixed with four times their bulk of alcohol sp. gr. 808 (or 95 per cent.), a solution of potassa in the same strength of alcohol was added, and the fluid was left for twelve hours to allow the potass-sugar to deposit itself. The liquid was then poured off; the deposited matter was dissolved in water, and tested by Trommer's test, Böttger's test, and a solution of potassa alone. No conclusive result was obtained.

Three other experiments were then made with 1,000 c. c. of urine and alcohol of the same strength. The copper test gave a decided reduction; the potassa alone hardly deepened in colour. The bismuth test was not conclusive; on testing the deposit from the alcohol for uric acid, it was found to be present in considerable quantity. In the Medico-Chirurgical Transactions vol. 26, p. 215 (1843), I have shown that uric acid reduces the oxide of copper in Trommer's test. Hence the reduction obtained in these three experiments was no proof of sugar being present, and I determined to try whether, by using large quantities of urine, sufficient sugar could be precipitated to admit of the determination of its presence and amount by the saccharimeter.

3,000 c. c. of urine (about 5 pints) were added to 12,200 c. c. of alcohol (above 21 pints). This quantity was divided into three portions; potassa dissolved in alcohol was added to each portion before it was set aside to deposit the sugar-potassa. The precipitate was dissolved in water, neutralised with oxalic acid, filtered through animal charcoal, and concentrated on a water-bath to about one ounce (30 c. c.). The clear fluid was examined by the saccharimeter, but no trace of rotation could be observed.

In another experiment, 1,000 c. c. of fresh urine were mixed with 4,000 c. c. of alcohol, and treated in the same way; but no trace of rotation was observed.

Another series of three portions of 1,000 c.c. of urine each, was mixed with 12,000 c.c. of alcohol, sp. gr. 808. The smallest quantity of water was used for dissolving the potassa sugar; a very small quantity of animal charcoal was used for decolorising the solution, which was examined by the saccharimeter; but no rotation could be seen.

Failing thus to detect sugar by the saccharimeter, I used Pettenkoffer's test on fresh portions of urine.

200 c. c. were mixed with alcohol and treated with potassa. A very small quantity of cholalic and of cholic acids was dissolved in concentrated sulphuric acid, and some of the fluid thought to contain sugar was added, but no purple tint in either case was produced. The test failed to find sugar, though the same solutions detected 2 milligrammes of sugar (·03 of a grain) dissolved in 10 drops of water, and one drop of diabetic urine, containing ·05 grain of sugar, gave a fine purple colour. As it was possible that by using a larger quantity of urine, some trace of sugar might be found, 3,000 c. c. of urine were precipitated by alcohol. The deposit was dissolved in a very small quantity of water and decolorized by animal charcoal, but no decided evidence of sugar was obtained.

At the time when these experiments were made with the alcohol process, I did not know how little sugar was precipitated by potassa from 80 per cent. alcohol. As this process failed, the lead process was tried.

On the detection of sugar in healthy urine by Brücke's lead process.

200 c. c. of healthy morning urine, passed by A, were treated

with lead and ammonia; the basic acetate of lead precipitate was dissolved in a small quantity of potassa, and the solution was tested with Fehling's standard-copper solution; no reduction was obtained, but the blue colour of the copper solution disappeared, and the liquid became of a light amber colour, but not a trace of suboxide of copper was seen. The ammonia precipitate was treated in the cold with oxalic acid, and the filtrate was examined for sugar by the copper solution, but no reduction occurred.

200 c. c. of mid-day urine (A) were treated exactly in the same way, and with exactly the same results.

500 c. c. of healthy urine (A) treated in the same way with oxalic acid gave no decided evidence of sugar by reduction, or by Pettenkoffer's test. This experiment repeated with another quantity of urine gave the same result. When in another experiment, the ammoniacal precipitate was decomposed by sulphuretted hydrogen, decided evidence of reduction was obtained.

1,000 c. c. of same urine (A) treated with oxalic acid instead of sulphuretted hydrogen, gave a reduction which was not sufficiently distinct. When this experiment was repeated and sulphuretted hydrogen employed, a distinct reduction of the oxide of copper took place, and Pettenkofer's test also showed that sugar was there. This last experiment was three times repeated, and reduction always occurred.

1,000 c. c. of the urine of another healthy man, (B) was treated in the same way by lead and sulphuretted hydrogen; the clear filtrate was evaporated and it reduced the copper solution readily.

2,000 c. c. of the urine (A) gave a very plentiful reduction. The experiment was repeated; the filtrate from the sulphide of lead was evaporated to dryness, and extracted with absolute alcohol; potassa-alcohol was then added; and a deposit formed on standing, which gave a good reduction.

It was requisite to prove that the reduction was caused by sugar. For this purpose, larger quantities of urine were treated in the same way, and the ammonia precipitate was tested for sugar by the saccharimeter and by fermentation.

5,000 c. c. of urine (A) were examined; the filtrate from the sulphide of lead was evaporated in vacuo; and the residue dissolved in a little water was decolorised by a little animal charcoal; half the solution examined by the saccharimeter gave 4° of rotation. In two other experiments with different quantities of the urine (A), 2° and 3° degrees of rotation were observed.

5,000 c. c. of urine (B) treated in the same way gave 5° of rotation.

1,100 c. c. of the urine of a third person (C) treated in the same way, gave 1½° of rotation; and by the reduction-test sugar was easily found.

In two experiments with 10,000 c. c. of urine (A) treated with oxalic acid, the decoloration could not be made so as to allow of the use of the saccharimeter; but the reduction-test and Pettenkofer's test gave full evidence of sugar.

Hence, in those different healthy persons, and in six different experiments, the rotation showed that sugar was present in the urine.

On the amount of rotation observed in healthy urine.

Two more experiments were made with the urine of (A) and (B), to determine the greatest amount of rotation in health.

5,000 c. c. of the urine (A) were treated as before with sulphuretted hydrogen. The whole of the fluid was used in the saccahrimeter, and the rotation was between 7° and 8°.

5,000 c. c. of the urine (B), when all the fluid was used, gave from 10° to 11° of rotation.

On the proof of the presence of sugar in healthy urine by fermentation.

10,000 c. c. (10 litres) of the urine (A) were treated with sulphuretted hydrogen. The filtrate was evaporated, and half was fermented in two portions.

	1st Portion.	2nd Portion.
Yeast employed . .	31·22 grs.	29·30 grs.
Total carbonic acid given off	0·80 gr.	0·86 gr.
Carbonic acid from yeast .	0·43 gr.	0·41 gr.
Carbonic acid from sugar .	0·37 gr.	0·45 gr.

Hence total carbonic acid from sugar = 0·82 gr. = 1·68 gr. sugar; so that the total quantity thus obtained from 10 litres was 3·36 grs. sugar.

14,000 c. c. of urine (A), after the filtrate from the sulphide of lead was evaporated to dryness, had the sugar precipitated from absolute alcohol by potassa. The precipitate was dissolved in water, neutralised by hydrochloric acid and evaporated; the residue extracted by strong alcohol; the alcoholic solution again evaporated to dryness; and the residue again dissolved in water, mixed with yeast which had been well washed, and kept at a temperature between 25° and 30° C.: (77° and 86°) F. in half an hour it began to ferment.

Yeast employed in sugar-solution . .	34·2 grs.
Carbonic acid given off	1·8 gr.
Yeast without sugar-solution . .	109·6 grs.
Carbonic acid given off	0·3 gr.

Therefore carbonic acid in 34·2 grs. of yeast may be neglected.

The yeast alone mixed with water and distilled, gave a scarcely perceptible trace of reduction when the distillate was added to a solution of chromic acid, whereas the other yeast-mixture distilled gave a fluid which showed plentiful reduction, proving that alcohol was present after fermentation.

The total carbonic acid given off = 1·8 gr.; this corresponds to 3·7 grs. sugar obtained from 14 litres of healthy urine.

An undetermined quantity of the different fluids which had been used in the experiments with the saccharimeter was evaporated; the residue extracted with strong alcohol; the alcoholic solution evaporated; the residue again redissolved in strong alcohol; and the solution was evaporated to dryness, dissolved in water, and mixed with slightly washed yeast.

Yeast used	44·6 grs.
Carbonic acid . . .	2·4 grs.

Yeast without sugar-solution 100·3 grs.; carbonic acid 0·7 gr. Hence 44·6 yeast give 0·3 gr. carbonic acid.

Hence carbonic acid from sugar = 2·4 grs. − 0·3 = 2·1 grs. = 4·3 grs. sugar.

The fluid distilled from yeast alone reduced chromic acid; the fluid which was distilled from the other apparatus reduced the chromic acid much more decidedly.

On the determination of the amount of sugar present in healthy urine.

Although the saccharimeter and fermentation afford the most satisfactory proof of the presence of sugar, yet the quantitative determination by either of these methods is not so accurate or so useful as by means of Fehling's standard-copper solution; because the processes for decolorising and for separating the sugar from the urine cause a great loss, which does not occur when the amount of sugar is determined by a standard solution, because then a smaller quantity of urine will give conclusive results.

1,000 c. c. (1 litre) of urine (A) was treated as before; the filtrate from the sulphide of lead was evaporated on a water-bath, decolorised with a little animal charcoal, and then tested by Fehling's solution.

The volume of fluid was 29 c. c.; of this 15 c. c. were required to reduce 10 c. c. of Fehling's solution. Hence the 29 c. c. contained 0·09 gramme sugar = 1·4 grain, as by the process one-third of the sugar present is lost. The litre contained about 2·2 grs. of sugar.

In another litre (A) the volume of fluid was 18 c. c.; of this 12 c. c. reduced 10 c. c. of Fehling's solution. Hence 18 c. c. contained 0·07 gramme sugar = 1·08 gr. Adding one-third to this, we find that the litre contained about 1·5 grains.

In another litre (A) the volume of fluid was 18 c. c.; of this 13 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·06 gramme sugar = ·924 gr. One-third added = 1·38 gr. to litre urine.

In another litre (A), the volume of fluid was 18 c. c.; of this 11 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·08 gramme sugar = 1·23 gr. One-third added = 1·8 gr. sugar to litre urine.

A litre of urine (B) was treated in the same way. The volume of fluid was 18 c. c.; of this 7 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·13 gramme sugar = 2·0 grs. One third added = 3·3 grs. sugar to litre urine.

In another litre (B), the volume of fluid was 26·6 c. c.; of this 12·6 c. c. reduced 10 c. c. of standard solution. Hence the 26·6 contain 0·1 gramme sugar = 1·5 gr. One-third added = 2·3 grs. sugar to litre urine. By the saccharimeter also evidence of rotation was obtained.

Hence,	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.
1 litre (A) urine contained	2·2 grs.	1·54	1·38	1·8 gr. sugar.
1 litre (B) urine contained	3·0 grs.	2·3 grs. sugar.		

From these experiments on healthy urine it follows:—

1. That by the alcoholic process, when 140 c. c. to 3,000 c. c. of urine were employed, no result was obtained by the reduction test, by Pettenkofer's test, or by the saccharimeter, chiefly because the percentage of alcohol was not great enough.

2. That by the lead process, most conclusive results were obtained, qualitatively and quantitatively, by the reduction test, by fermentation, and by the saccharimeter.

By the reduction test, qualitatively, 200 c. c. of urine gave no evidence; 500 c. c. failed, and 500 c. c. gave proof of sugar; 1,000 c. c. gave very evident sugar; 3,000 c. c. gave much more proof. By this test, quantitatively 1,000 c. c. of one man gave 2·2, 1·5, 1·4, and 1·8 grs. of sugar. The same quantity of urine in another man gave 3·0 and 2·3 grs. of sugar in one litre.

By the saccharimeter, quantitatively, 5,000 c. c. of urine, partly used, gave 2°, 3°, and 4° of rotation. In another man, 5° were observed. In a third man, a smaller quantity of urine gave 1° to 2° of rotation.

By this test quantitatively, 5,000 c. c. of one man, all used, gave 7° to 8° of rotation. The same quantity from another man, gave 10° to 11°.

By fermentation, qualitatively, an unknown quantity fermented, gave distinct evidence of alcohol and 2·1 grs. of carbonic acid.

Quantitatively, 10,000 c. c. of urine were used, and ultimately, 1·64 gr. of carbonic acid was obtained.

14,000 c. c. of the same urine gave most positive proof of alcohol and 1·8 gr. of carbonic acid.

These experiments, therefore, fully confirm Professor Brücke's statement, that sugar exists in healthy urine. By obtaining alcohol from the fermented fluid, and by never failing to find rotation when the saccharimeter was used, provided sufficient urine had been taken for the experiments, I have added to the evidence given in his original paper.

III.—*Analysis of the Saline Water of Purton, near Swindon, North Wilts.*

By Henry M. Noad, Ph.D., F.R.S., and C.S.

The water rises in a field on the Oxford Clay, which reaches from the bottom of the hill on which the village of Purton is built, to the river Thames at Cricklade, a distance of about three miles, the spring being about midway between both. The soil of Purton rests on the limestone. The field in which the spring rises has long been known in the neighbourhood as "Salt's Hole." The medicinal properties of the water are held in high esteem by the inhabitants of Purton, and the proprietor has recently erected a pump-room round the well, from which about 120 gallons of the water can be pumped up daily.

The water, which was analysed at the request of Dr. Kinneir, of Purton, was collected by myself in the month of January in the present year. As pumped up from the well, it was quite clear, and remained so after long standing. While the pump was in action, a faint but decided smell of sulphuretted hydrogen was perceptible, but the water itself, while still, had no such odour.

The temperature of the water was nearly the same as that of the air. Specific gravity, at 60°F., = 1·0056. Free carbonic acid, 50 cubic inches per imperial gallon, the water being slowly pumped up from the well.

The analysis was performed in the usual manner, the iodine, which could be distinctly recognised in one pint of the water, being estimated as *protiodide of palladium.*

In the arrangement of the results of analysis, the strongest acid is assumed to be combined with the strongest base; and the lime and magnesia thrown down as carbonates by boiling, are considered as existing in the water as carbonates held in solution by carbonic acid.

Direct results of analysis calculated to 1 imperial pint.

BASES.

Experiment.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.........	6·422	4·748	18·90	1·179	17·721
II.........	6·257	4·783	19·33	1·020	18·310
Mean	6·340	4·765	19·10	1·099	18·016

Acids

(or elements replacing them).

Experiment.	Sulphuric Acid.	Chlorine.	Iodine with traces of Bromine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid as Carbonate of Lime and Carbonate of Magnesia.	Carbonic Acid, free.	Phosphoric Acid.	Apocrenic Acid.
I....	24·00	2·82	”	0·27	”	2·38	”	”	”
II....	23·80	2·80	”	0·29	”	2·36	”	”	”
Mean	23·90	2·81	0·0094	0·28	5·403	2·37	3·133	0·031	0·112

Verification for Lime.

Experiment.	Lime precipitated by boiling.	Lime left in solution after boiling.	Total by Calculation.	Total by Experiment.
I.	2·828	3·280	6·108	6·422
II.	2·857	3·310	6·077	6·257
Mean	2·842	3·296	6·092	6·340

Verification for Magnesia.

Experiment.	Magnesia precipitated by boiling.	Magnesia left in solution.	Total by Calculation.	Total by Experiment.
I	0·11	4·735	4·845	4·748
II	0·15	4·785	4·945	4·783
Mean	0·13	4·755	4·890	4·765

RESIDUE LEFT ON EVAPORATION.

Experiment.	Mineral Residue.	Organic Residue.	Total Residue.
I	51·02	0·114	51·114
II	51·21	0·110	51·320
Mean	51·11	0·112	51·217

Solid Contents of an imperial pint as determined by analysis.

Carbonate of lime	5·0760
Carbonate of magnesia	0·2630
Lime (not as carbonate)	3·2200
Magnesia (not as carbonate) . . .	4·7580
Potash	0·6930
Soda	9·5460
Chlorine	2·8100
Sulphuric acid	23·9000
Silica	0·2800
Phosphoric acid	0·0310
Bromine	traces
Iodine	0·0094
Crenic acid	traces
Apocrenic acid	0·1120
	50·6984
Residue left on Evaporation . .	51·2170

Saline Constituents in one Imperial Gallon.

Carbonate of lime	40·608
Carbonate of magnesia	2·104
Sulphate of potash	10·264
Sulphate of soda	174·904
Sulphate of lime	62·560
Sulphate of magnesia	76·592
Chloride of magnesium	30·000

Iodide of sodium	0·088
Silica	2·080
Phosphoric acid	0·248
Crenic acid	traces
Apocrenic acid	0·896
Bromine	traces
	400·344

IV.—*On the Composition of Purton Saline Water.*

BY AUGUSTUS VOELCKER, PH. D.

(PROFESSOR OF CHEMISTRY IN THE ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.)

NOTICING that Dr. Noad intends reading on the 17th December, 1860, a paper on the analysis of Purton saline water, I beg likewise to communicate an analysis of that water, which I made for the proprietor in October, 1859.

The following are the direct results of the analysis. An imperial gallon contains:—

	Grains.
Organic matter and water of combination (being loss obtained on heating residue, dried at 320°F)	8·750
Lime	34·536
Magnesia	25·736
Oxides of iron and alumina, with traces of phosporic acid	·280
Potash	20·707
Soda	49·006
Chloride of sodium	34·297
Sulphuric acid	165·074
Soluble silica	1·280
Iodine	0·056
Bromine	·080
Carbonic acid	33·090
Sulphuretted hydrogen	traces
Specific gravity of water	1·0045

These constituents arranged into compounds give the following results:—

	Grains per imp. gal.
Organic matter and water of combination (loss on drying residue at 320°F)	8·750
Sulphate of soda	112·239
Sulphate of magnesia	77·208
Bromide of magnesium	·092
Iodide of sodium	·066
Chloride of sodium	34·297
Sulphate of lime	83·873
Sulphate of potash	1·916
Carbonate of potash	28·880
Oxides of iron and alumina with traces of phosphoric acid	·280
Silica	1·280
Solid residue, dried at 320°F per imperial gallon	348·881
Free carbonic acid	23·820

Dr. Noad has communicated his results to me. They differ materially from mine. But the fact that the water analysed by Dr. Noad contains a great deal more solid matter than the water analysed by me, shows sufficiently that we examined two different specimens of Purton water. I have determined at various times the amount of residue which is left on evaporation, and find great differences in the total amount of total saline matters. Probably the composition of the saline residue varies at different seasons, and the water, like other saline waters obtained only in limited quantities, is not always of the same composition.

With respect to the arrangement of the direct results of the analysis into compounds, I beg to observe that I have purposely united carbonic acid with potash and not with lime. In his arrangement of results, Dr. Noad does not give any alkaline carbonates. The Purton water, which I examined, however, contains alkaline carbonates, for it exhibits a strong alkaline reaction to litmus paper, even before evaporation.

It is of course impossible to say what proportions of the carbonic acid and sulphuric acid are united with lime and the alkalies, and I have deviated from the ordinary mode of uniting acids and bases together, because the Purton water in its natural condition really contains alkaline carbonates.

V.—*On the Basic Carbonates of Copper, with some Remarks upon the Carbonates of Nickel and Cobalt.*

By Frederick Field.

In a paper upon this subject, lately published in the "Chemical News," and in Abstract at page 70 of this volume, the singular effect of a strong solution of carbonate of soda upon malachite was mentioned, together with the action of boiling water upon the same mineral. In both instances it speedily becomes black, being converted into the black oxide, with brisk evolution of carbonic acid. When the blue carbonate of copper (azurite) $3CuO.2CO_2.HO$ is subjected to similar treatment, exactly the same phenomenon occurs, the whole of the carbonic acid being expelled, the action of pure water facilitating the decomposition far more readily than the solution of carbonate of soda. In a memoir upon the carbonates of copper, Rose[*] informs us, that the green carbonate formed on adding a salt of copper to carbonate of soda, is converted into the oxide by long digestion with boiling water, but no blue compound is obtained. Artificial malachite may, however, be formed from azurite, by heating the latter for some little time in a rather concentrated solution of bicarbonate of soda. A bright blue liquid is produced, which, after lengthened ebullition, deposits a green powder, containing exactly the amount of oxide of copper which is found in malachite; it is this precipitate, which has a similar composition to that which is produced by boiling a solution of malachite in carbonate of soda, does not part with its water under a temperature of 380° F, and is evidently formed by the elimination of 1 atom of carbonic acid from 2 atoms of azurite, one atom of water at the same time taking the place of the carbonic acid—

$$2\ (3CuO.\ 2CO_2.\ HO) - CO_2 + HO = 3\ (2CuO.\ CO_2.\ HO)$$

Deville[†] mentions that when a salt of copper is gradually added to a strong solution of carbonate of soda, nearly the whole of the alkali is precipitated with the copper, in brilliant crystals of the double carbonate. In all my experiments, warm solutions were employed, in which case no double compound was formed, but a highly basic carbonate, and subsequently black oxide, were alone produced.

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[*] Pogg. Ann. lxxxiv, 461; Ann. Ch. Pharm. lxxx, 236.

[†] Ann. Ch. Phys. [3], xxxiii, 75

Carbonate of Cobalt. The various carbonates of cobalt have been intimately studied by Rose,* who remarks that the composition of these compounds depends very much upon the concentration of the solutions, and upon the temperature employed during the precipitation. When sulphate of cobalt is mixed with carbonate of soda, a precipitate is formed having the formula $2(CoO. CO_2) + 3(CoO. HO) + Aq.$, either from concentrated or from weak solutions, and it is only when dilute solutions are decomposed at the boiling point, that a precipitate is obtained which approximates to $CoO. CO_2 + 2(CoO. HO), Aq.$ The same chemist further informs us, that when sulphate of cobalt is treated with an excess of bicarbonate of potash in the cold, there is formed, with brisk evolution of carbonic acid, a voluminous precipitate, which by long standing is transformed into a mass of tolerably distinct crystals, having for their composition $KO. CO_2 + CoO. CO_2 + 9HO$. The rather curious phenomena exhibited by the addition of dilute copper-salts to a strong solution of carbonate of soda, the latter in great excess, led me to investigate the reaction induced upon the salts of cobalt under similar circumstances. When dilute nitrate of cobalt is added to bicarbonate of soda, no precipitate occurs, until a considerable quantity has been introduced. The solution has a beautiful violet colour, and can be brought to ebullition, and even maintained at a boiling temperature for some time without undergoing complete decomposition. The precipitate which forms after a further addition of the cobalt-salt, has a pure pink colour, which scarcely changes its tint, even when the liquid in which it is suspended is boiled for several hours. This compound appears to hold carbonate soda with remarkable tenacity; indeed it seems impossible to free it from the latter by any amount of ordinary washing. When the filtrate no longer shows signs of alkalinity to test-paper, the precipitate removed from the filter and heated with a fresh portion of distilled water, still yields an alkaline solution. On filtering off the carbonate of soda, and heating with water as just described, the pink colour quickly vanishes, and it becomes brown. When nitrate of cobalt is added to an excess of carbonate of soda, carefully freed from all excess of carbonic acid, the precipitate is not pink but blue, maintains its colour with some persistency as long as the supernatant liquid is strongly alkaline, and is quite as difficult to free from adhering soda as the other compound. Cobalt, it appears, differs somewhat from copper when acted upon by either the carbonate or the bicarbonate of soda. When a salt of copper, it may be remembered, is added to a strong hot solution of the former, immediate decomposition takes place, carbonic acid is evolved, and a highly basic carbonate formed, which is ultimately converted into the black oxide. When the bicarbonate is employed, a green precipitate of hydrated bicarbonate is obtained. In order to see if oxide of cobalt altogether free from carbonic acid can be procured by long-continued boiling in distilled water, solutions of the nitrate of that metal and carbonate of soda were mixed, neither being in great excess. The peach-coloured compound was well washed and suspended in a pint of water, which was brought to ebullition and maintained at that temperature for about ten hours, water being added from time to time to compensate for the loss resulting from evaporation. The precipitate soon changed colour, becoming brown, and ultimately black. After filtration, it was dried at 212° Fah. and analysed, yielding 12·34 of carbonic acid, and 78·51 black oxide of cobalt (Co_3O_4) upon intense ignition. The carbonate of cobalt, as it originally existed, was composed of $2(CoO.\ CO_2)\ 3(CoO.\ HO) + Aq.$, and by the action of water at 212°, parted with a portion of its carbonic acid, and became partially converted into the sesquioxide. A compound containing 12·21 carbonic acid, which upon ignition would yield 78·41 of the protoperoxide of cobalt, would have the following formula :—

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* Pogg. Ann. lxxxiv. 548. Ann. Ch. Pharm. lxxx. 237.

$$2\ (CoO.\ CO_2)\ 3\ (CoO.\ HO) + Aq + Co_2O_3,\ HO.$$

Found.	Calculated.
$CO_2 = 12·34$	CO_2 12·12
Co_3O_4 78·51	$Co_3\ O_4$ 78·41.

That this compound is a mixture of ordinary carbonate of cobalt with the hydrated sesquioxide, arises from the action of dilute hydrochloric acid. When this acid, diluted with three or four times its bulk of water, is added to the carbonate, the latter is almost instantaneously dissolved, with brisk disengagement of carbonic acid. Upon the sesquioxide, however, it produces little effect. When cold and comparatively weak, the liquid becomes only slightly tinged, after being in contact with it many hours. Exactly the same phenomena occour in the compound just mentioned. On the addition of dilute hydrochloric acid, the whole of the carbonate is immediately dissolved, a black powder remaining untouched. When warm and concentrated acid is added to this, it is gradually decomposed, solution is effected, and chlorine is evolved. When nitrate of cobalt is added to a solution of bicarbonate of soda containing a small quantity of the hypochlorite of that alkali, an intense and beautiful green colour is produced, and no elimination of carbonic acid results. So strong is the colouring power of this body, that 0·2 of a grain of nitrate of cobalt will colour eight ounces of solution, a clear bright green, as dark as a tolerably concentrated solution of chloride of copper. Large quantities of oxide of cobalt can be dissolved in this way, and the liquid, if not too strong, may be boiled for some time without undergoing decomposition. When, however, the nitrate of cobalt is rather concentrated, and heat is applied, a brisk evolution of carbonic acid takes place, and sesquioxide is precipitated, which, adhering in a scaly mass to the sides of the glass, and being removed by agitation, floats about the liquid in brilliant iridescent plates, appearing at first sight to be beautifully and highly crystalline.

Cobalt cannot be separated from iron or manganese by this method, although every degree of concentration and temperature has been tried. When the solution is not sufficiently warm, a small quantity of iron is dissolved, when, on the other hand, considerable heat is applied, a small quantity of cobalt remains with the precipitate.

Carbonates of Nickel. Nickel-salts exhibit, generally speaking, the same reactions as those of cobalt in excess of carbonate of soda. I have tried in vain to procure oxide of nickel perfectly free from carbonic acid by boiling the carbonate in water, although the resulting compound was very highly basic. No peroxide however is formed, as in the case of cobalt. The carbonates of nickel, when precipitated in very strong solutions of the alkaline carbonates, appear to hold the latter with as great tenacity as the cobalt-compound.

VI.—*Preliminary Note concerning a new Homologue of Benzoic Acid.*

By Arthur H. Church, B.A.

Attempts have been made to effect the oxidation of benzol by means of an oxidizing mixture consisting of bichromate of potassium and sulphuric acid; it has been found, however, that the hydrocarbon remained unattacked. Not so, however, with the other members of the same series, toluol and cumol yielding benzoic acid, and cymol, an acid of totally different properties and constitution. I have succeeded in producing from benzol an apparently new oxygenated body, presenting all the properties one might expect to find in a homologue of benzoic acid containing CH_2 less than that substance. This supposition is strengthened by the result of an experiment in which nitrobenzol was made to yield an acid body apparently standing in the same relation to the first-mentioned new acid as nitrobenzol to benzol.

The following was the plan pursued in the preparation of the new acids: Pure benzol was dissolved in a slight excess of Nordhausen sulphuric acid, and the mixture heated for some time to 100° C. It was then diluted with about its bulk of water, and transferred to a retort. Small fragments of bichromate of potassium were added gradually to the liquid, the temperature of which was slowly raised. The acid was found partly floating on, and partly dissolved in, the aqueous distillate. Great care must be taken lest the oxidation proceed too actively, and the product be lost. The acid is a white fusible and crystalline solid, distinguished from Collinic acid, to which the same formula has been assigned, by its far greater solubility in hot water. The analytical results indicate the formula—

$C_6H_4O_2$* for the acid; and
$C_6H_3MO_2$ for the salts.

The fact that benzol is reproduced in large quantity from sulphobenzolate of ammonium $C_6H_5 . NH_4 . SO_3$, when that salt is submitted to dry distillation, suggested the probability that the acid itself, when acted on by an oxidizing agent, might yield the products which we should expect to obtain by the oxidation of the original benzol.

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* C = 12; O = 16; S = 32; H = 1.

When sulphotoluolic and sulphocumolic acids are similarly treated, benzoic acid is the corresponding product: with sulphocymolic acid, a white powder, apparently identical with the insolinic acid of Hofmann, is obtained.

Nitrobenzol is attacked with the utmost difficulty by the chromic acid mixture. By long boiling it is, however, at length converted into a white acid, which crystallizes from boiling water in large nacreous plates. Analysis has led to the formula—

$C_6H_3(NO_2)O_2$ for the acid; and
$C_6H_2(NO_2)MO_2$ for the salts.

Nitrotoluol and nitrocumol are oxidized with considerable ease under similar conditions, yielding nitrobenzoic acid in abundance. This is the case also with nitrosulphotoluolic acid, $C_7H_6NO_2 . H . SO_3$, the acid sulphite of nitrotoluenyl.

The acid from nitrobenzol was obtained in June last, but MM. Cloëz and Mignet announce in the "Comptes Rendus" of January 21st, 1861, that they have obtained a new acid from nitrobenzol by oxidizing it with permanganate of potassium or with a mixture of bichromate of potassium and nitric acid. To their acid they assign the expression—

$$C_9H_7(NO_2)O_3,$$

But it is not easy to see how such a body can be derived from the oxidation of nitrobenzol, which contains only C_6. Indeed the authors are by no means certain of the purity of the nitrobenzol which they employed, and they even go so far as to suggest that the acid which they describe may have owed its origin to some foreign body with which the commercial nitrobenzol on which they operated may have been contaminated.

VII.—*On some products of the Action of Dilute Nitric Acid on some Hydrocarbons of the Benzol Series.*

(PRELIMINARY NOTICE.)

By Warren DeLaRue, Ph. D., F.R.S., etc. and
Hugo Müller, Ph. D., F.C.S.

Some years ago, whilst investigating the nature of Burmese naphtha, and examining the products of the action of nitric acid on the hydrocarbons obtained therefrom, our attention was directed to similar experiments made many years ago by Laurent, who discovered, amongst the products of the action of nitric acid on coal-tar naphtha and the naphtha obtained by distilling bituminous schist, a new acid called *ampelic acid*, of the interesting composition $C_7H_6O_3$,* being isomeric with salicylic acid. As we failed to find ampelic acid amongst the products resulting from the action of nitric acid on Burmese naphtha, we repeated Laurent's experiments with coal-tar naphtha, but with no better result; we could detect no substance corresponding with his description of ampelic acid. These experiments with coal-tar naphtha, in consequence of their giving a negative result with regard to ampelic acid, occupied our attention for some time, as we were desirous of making out the somewhat complex nature of the products resulting from the long-continued action of nitric acid on this particular class of hydrocarbons. The coal-tar naphtha used consisted principally of toluol, xylol, and pseudocumol.

Reserving for a further communication the details of our investigation, we will simply state at present that we finally succeeded in obtaining four different acids of the aromatic series. The interest attaching to some of them may justify the bringing of our results in an incomplete form under the notice of the Society, and we are the more induced to take this step, because we believe that other chemists are directing their attention to similar products. The preparation and separation of the substances under consideration is attended with the expenditure of a considerable time, and the completion of our researches may consequently be somewhat delayed.

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* Carbon = 12; Oxygen = 16; Hydrogen = 1.

For our experiments we distilled in a capacious retort, purified coal-tar naphtha with about 15 times its volume of dilute nitric acid (containing 1 volume of commercial acid to 3 volumes of water). The action of the acid is very slow; but after several days, the hydrocarbons are changed into a heavy liquid which gradually becomes converted into a yellowish-white flocculent substance, partly suspended in the acid and partly dissolved in it. When no further change is perceptible, the retort is allowed to cool. The resulting yellowish-white substance is separated by filtration from the acid mother-liquor, and treated with a large quantity of boiling water, which dissolves the greater part, and leaves some semi-liquid nitro-compounds, and a few other substances undissolved. On cooling, the aqueous solution deposits the white substance it had held in solution. For the purpose of separating the adhering nitro-compounds and nitro-acids, the white substance is dissolved in ammonia, mixed with sulphide of ammonium, and boiled until the nitro-compounds are converted into amidogen-compounds. To the resulting deep-red solution are then added a few drops of hydrochloric acid, which causes a brown precipitate of the amidogen-compounds, separable by filtration. The filtrate is then completely precipitated by a further addition of hydrochloric acid, and the precipitate, consisting of several acids, is then filtered off and treated again with a large quantity of boiling water, which leaves undissolved an insoluble acid. The substance deposited on cooling is filtered off and dried. After having been previously fused, it is introduced into a small retort and then submitted to careful distillation. At first there distils over a colourless liquid, which very soon solidifies, like palmitic acid, in the neck of the retort. After a certain time, a new substance makes its appearance and crystallizes in large acicular crystals in the bulb of the retort, just above the boiling liquid. The distillation is stopped at this point; and after cooling, the first-named substance in the neck of the retort is removed by gently warming it. On subsequently continuing the distillation, very little passes into the neck of the retort, the residue becoming gradually black and solid, whilst the upper part of the bulb becomes filled with magnificent crystals. When the formation of the latter ceases, the operation is discontinued. The palmitic-acid-like distillate is a mixture of two acids, and for the purpose of separating them, it is powdered and brought into contact with purified Burmese naphtha boiling at about 90° C. (probably hydruret of capryl C_8H_{18}). The hydrocarbon extracts one part of the distillate, leaving the other undissolved. After the hydrocarbon has been filtered, it is distilled, whereon a liquid residue remains in the retort, and gradually solidifies to a beautiful crystalline mass. This crystalline substance is an acid possessing the general properties of benzoic acid. A combustion made with material not quite free from the second acid (which we succeeded at last in separating completely with Burmese naptha, which we had not employed in our first experiment), gave numbers ($C_6H_4O_2$), approaching very nearly those of the next lower homologue of benzoic acid. This new acid fuses at about 60° C., but occasionally remains liquid, even at the ordinary temperature, especially when not quite pure. It is heavier than water, and mixes in all proportions with alcohol; it is only slightly soluble in cold water, but more so in boiling water. From a saturated hot solution it separates, whilst the solution is cooling, as a heavy oil which sometimes solidifies immediately, but at other times only after a certain interval. This acid is slightly volatile, even at ordinary temperatures, for it covers itself with beautiful crystallizations. It possesses a very acrid taste. When boiled with water, it volatilizes to a considerable extent. It can be distilled *per se* without decomposition, and forms well-crystallized salts with the alkalies. From this description it will be perceived that this acid bears a great similarity to an acid which was described only a few months since by Fröhde, who obtained it, in small quantities amongst the products of oxidation of glue and albuminous substances, and called it accordingly *Collidinic acid.* The difference which still exists may be cleared up by further investigation; for Fröhde had not material enough for combustion, nor was his acid quite free from benzoic acid. Although the quantity of this acid formed from the hydrocarbons is not great, we have no doubt that this source will furnish the material for a complete investigation of this highly interesting acid.

The acid which is left undissolved by the Burmese naphtha (hydruret of capryl) has the composition of benzoic acid, but it differs in some points from the true benzoic acid, wanting its great power of crystallization. It seems not unlikely that this acid is identical with *salylic acid* the isomer of benzoic acid quite recently described by Kolbe and Lautemann ($C_7H_6O_2$).

The before-named crystalline sublimate which deposits in the bulb of the retort is an acid which differs considerably from any of the known acids. In its chemical properties it resembles closely terephthalic acid, but it differs from this acid in its capability of forming large and distinct crystals when it is sublimed. The crystals when obtained by sublimation form arborescent masses of large prismatic crystals. The quantity of the acid obtained was too small to ascertain its chemical nature more fully.

Lastly, the insoluble acid, which remains undissolved when the precipitate is obtained by the addition of hydrochloric acid to the ammoniacal solution of the crude acids, after treatment by sulphide of ammonium, is principally *terephthalic acid* ($C_8H_6O_4$).

The terephthalic acid is dried and converted into terephthalic chloride, which, when heated with methylic alcohol, furnishes terephthalate of methyl, which can be readily purified by re-crystallization from alcohol, and thus when decomposed offers a ready means of procuring terephthalic acid in a pure state.

VIII.—*On the Bisulphide of Iodine.*

By Frederick Guthrie.

An examination of the action of certain compound halogens on some of the olefines, has led me to consider incidentally the preparation of some of the compound halogens in the pure state.

Of compound halogens, while the constitution of none is more invariable and definite than that of the bisulphide of chlorine,—the bisulphide of iodine can scarcely be said to have been prepared, notwithstanding the strong analogy between chlorine and iodine.

That iodine combines with sulphur is well known; that such combination is attended by the liberation of heat is equally well established; and since homogeneous mixtures of the two may be prepared in all proportions, it is clear that a substance having the percentage composition of the bisulphide of iodine may be formed. Bodies so formed have little or no title to the name of chemical compounds.

If we remember, on the one hand, the fact which I have abundantly proved on former occasions, that an equivalent of bisulphide of chlorine functions as two equivalents of chlorine, or, as some chemists would express it, that the molecule of bisulphide of chlorine is biatomic; and if we further remember that at least two equivalents of chlorine or of zinc are required to *recompose* iodide of ethyl, according to the equations—

$$(1)^* \quad C_4H_5I + 2Cl = C_4H_5Cl + ICl$$

$$(2) \quad C_4H_5I + 2Zn = C_4H_5Zn + ZnI$$

we must be prepared to anticipate the analogous re-action—

$$(3) \quad C_4H_5I + S_2Cl = C_4H_5Cl + S_2I:$$

This the more, because in the case of certain compounds, such as NaSn, we find—

$$(4) \quad C_4H_5I + NaSn = C_4H_5Sn + NaI.$$

The method I employ for the preparation of the bisulphide of iodine is in fact based upon the validity of equation (3).

Recompositions quite akin to (3) are suffered by the iodides of methyl and of amyl; whence we may assert the general equation—

$$(5) \quad C_nH_{n+1}I + S_2Cl = C_nH_{n+1}Cl + 3_2I.$$

For obvious reasons the ethyl-compound is preferred.

The reciprocal action of iodide of ethyl and bisulphide of chlorine is perhaps as interesting in its manner as in its result. The two liquids may be mixed in all proportions without a greater change in colour than is due to the dilution of the coloured sulphide by the colourless iodide; neither is heat liberated nor other immediate token given of chemical change taking place. The change appears to be complete in about twelve hours. If the vessel be open to the air, the chloride of ethyl evaporates as it is formed, leaving the bisulphide of iodine in magnificent crystals, contaminated, however, by the products of the action of the moisture of the air upon the bisulphide of chlorine. For this reason the process is best conducted in a hermetically sealed tube. The co-reagents are used in the proportions shown by the equation—a very slight excess of the iodide being added.

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* Equation (1) expresses only the initial recomposition—the ultimate products are HCl, ICl_3 and chlorine substitution-products of C_4H_5Cl.

On opening a tube so charged, which has been left over night, and applying the heat of the hand, the chloride of ethyl escapes. A gentle heat suffices to expel the residual iodide of ethyl—whereupon the bisulphide of iodine is left in the form of fine tabular crystals of the lustre of iodine and in a state of absolute purity.

Although the exact composition of the substance may be fairly deduced from its synthesis, it was submitted to analysis in the following way.

0·3270 grm. was heated in a combustion-tube with nitrate of potash and carbonate of soda, whereby the iodine and sulphur were converted respectively into iodide and sulphate of potassium. They were then estimated in the usual way:

	Calculated.	Found.
S_2	20·13	20·28
I	79·87	79·81
	100·00	100·09

Though in this note, this curious re-action is considered as a means of preparing the compound halogen S_2I, it is perhaps of equal interest as offering a method for preparing an organic chloride from its iodide;—a problem hitherto difficult and cumbrous in solution, albeit its inverse is often easy and of frequent occurrence.

On Azobenzol and Benzidine.

By P. W. Hofmann.

[From the Proceedings of the Royal Society for June, 1860.]

Among the numerous compounds into which benzol, when submitted to reagents, is converted, *azobenzol* and its derivatives have as yet received but limited attention. Although more than twenty-five years have elapsed since this interesting body was discovered by Mitscherlich, both its formation and its constitution remain still doubtful.

Mitscherlich*, who discovered azobenzol in 1834, when submitting nitrobenzol to the action of an alcoholic solution of potassa, represented this compound by the formula

$$C_6H_5N\dagger,$$

but left the reaction which gives rise to the formation of azobenzol unexplained. In 1845 this body was reprepared by Hofmann and Muspratt‡, who observed among the collateral products of the reaction *aniline* and *oxalic acid*. They represent the formation of azobenzol by the equation

$$2C_6H_5NO_2 + C_2H_6O = C_6H_5N + C_6H_7N + C_2H_2O_4 + H_2O,$$

Nitrobenzol. Alcohol. Azobenzol. Phenylamine. Oxalic acid.

adding at the same time that they are far from considering this equation as more than the representation of *one* phase of the transformation of nitrobenzol, since several other rather indefinite compounds are formed simultaneously.

At about the same period Zinin made the interesting observation that azobenzol is capable of fixing hydrogen and of being thereby converted into a well-defined base, benzidine, which he represented by the formula

$$C_6H_6N.$$

Considering the physical characters both of azobenzol and of benzidine, especially the high boiling-points of these substances, and the ratio of hydrogen and nitrogen in the latter compound, the sum of the number of equivalents of these two elements not being divisible by 2, many chemists were inclined to double the formulæ of both bodies, and to represent them by the following expressions:—

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* Pogg. Ann, xxxii. p. 224.

† $H=1$, $O=16$, $C=12$, &c.

‡ Mem. of the Chem. Soc. vol. iii. p. 113.

Azobenzol ...... $C_{12}H_{10}N_2$
Benzidine ...... $C_{12}H_{12}N_2$

This view received the first experimental confirmation in the formation of the nitro-derivatives of azobenzol, which were examined in 1849 by Gerhardt and Laurent. The formation of

Nitrazobenzol.... $C_{12}H_9N_3O_2=C_{12}[H_9(NO_2)]\ N_2$,
Dinitrazobenzol.. $C_{12}H_8N_4O_4=C_{12}[H_8(NO_2)_2]N_2$,

and of several derivatives of these bodies, having established the C_{12}-formula of azobenzol, but little doubt could be entertained regarding the formula of benzidine, which is as readily obtained from azobenzol by reducing agents, as it may be reconverted into azobenzol by nitric acid*.

The molecular value of benzidine being thus almost exclusively fixed by the determination of the formula of the compound from which it originates, it was of some interest to obtain additional experimental evidence for the molecular weight of azobenzol.

With this view I have determined the vapour-density of azobenzol. This body boiling at a rather high temperature, I have availed myself of the method of displacement lately proposed by Professor Hofmann. Experiment proved the density of the azobenzol-vapour to be 94 referred to hydrogen as unity, or 6·50 referred to air. The theoretical vapour-density of azobenzol, assuming that one molecule of this compound furnishes, like the rest of well-examined substances, 2 vols. of vapour†, is $\frac{182}{2}=91$ referred to hydrogen, and 6·32 referred to air.

This determination of the vapour-density, then, plainly confirms the higher molecular weights proposed for azobenzol and for benzidine.

When determining the vapour-density of azobenzol, I had occasion to observe that, probably in consequence of a typographical error, the boiling-point of this compound is misstated in all the manuals which I could consult, and even in the original memoirs of Mitscherlich himself. The boiling-point is stated to be 193° C., whilst it is in reality 293° C.

Benzidine, when expressed by the formula

$$C_{12}H_{12}N_2,$$

presents itself as a well-defined diacid diamine. The molecular construction of the diatomic base remained to be decided.

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* Noble, Journal of the Chem. Soc. vol. viii. p. 293.

† $H_2O=2$ vols.

I have endeavoured to solve this problem by the process of ethylation, as yet the simplest and the best guide in determining questions of this kind. Benzidine in the presence of alcohol is rapidly attacked by iodide of ethyl. After two hours' digestion at 100° C. in sealed tubes, the reaction is complete. The solution on evaporation yields a crystalline iodide,

$$C_{16}H_{22}N_2I_2=C_{12}H_{12}(C_2H_5)_2N_2I_2,$$

from which ammonia separates a solid crystalline base very similar to benzidine. This compound, which fuses at 65° C., and resolidifies at 60° C., is *diethylbenzidine:*

$$C_{16}H_{20}N_2=C_{12}H_{10}(C_2H_5)_2N_2,$$

which forms well-crystallizable salts with the acids, and yields with dichloride of platinum a difficulty soluble crystalline platinum-salt containing

$$C_{16}H_{22}N_2Cl_2,2PtCl_2.$$

When diethylbenzidine is treated again with iodide of ethyl, the phenomena previously observed are repeated. The iodide

$$C_{20}H_{30}N_2I_2=C_{12}H_{10}(C_2H_5)_4N_2I_2$$

is formed, which when decomposed by ammonia yields *tetrethylbenzidine*

$$C_{20}H_{28}N_2=C_{12}H_8(C_2H_5)_4N_2.$$

Tetrethylbenzidine resembles the diethylated and the non-ethylated base. It fuses at 85° C., resolidifying at 80° C., produces with the acids crystalline compounds, and furnishes with dichloride of platinum, a platinum-salt of the formula

$$C_{20}H_{30}N_2Cl_2,2PtCl_2.$$

The further action of iodide of ethyl upon tetrethylbenzidine is extremely slow. After 12 hours' digestion at 100° C. only a very minute quantity of the base had been transformed into an iodide. Iodide of methyl, on the other hand, acts with great energy. An hour's digestion is sufficient to produce the final diammonium-compound.

The iodide

$$C_{22}H_{34}N_2I_2=C_{12}H_8(C_2H_5)_4(CH_3)_2N_2L_2$$

is very difficultly soluble in absolute alcohol, but dissolves with facility in boiling water, from which it is deposited on cooling, in long beautiful needles. The solution of this iodide is no longer precipitated by ammonia, but yields with oxide of silver a powerfully alkaline solution, exhibiting all the characters of the completely substituted ammonium- and diammonium-bases discovered by Professor Hofmann. The solution of this dimethyl-tetrethylated base, which contains

$$C_{22}H_{36}N_2O_2=\left.\begin{array}{r}C_{12}H_8(C_2H_5)_4(CH_3)_2N_2\\H_2\end{array}\right\}O_2,$$

is not further acted upon by either iodide of ethyl or methyl. With acids it forms a series of salts which are remarkable for the beauty with which they crystallize. The platinum-salt is almost insoluble in water, but soluble with difficulty in concentrated boiling hydrochloric acid, crystallizing from this solution on cooling in beautiful needles. This salt contains

$$C_{22}H_{34}N_2Cl_2,\ 2PtCl_2.$$

The above experiments appear to establish the molecular construction of benzidine in a satisfactory manner. This base is obviously a primary diamine, in which the molecular group $C_{12}H_8$, whatever its nature may be, functions as a diatomic radical. A glance at the subjoined Table exhibits the construction of benzidine and of the several compounds which I have described.

Diamines.

Benzidine ......
$$\left.\begin{array}{c}(C_{12}H_8)''\\ H_2\\ H_2\end{array}\right\}N_2,$$

Diethylated benzidine ......
$$\left.\begin{array}{c}(C_{12}H_8)''\\ (C_2H_5)_2\\ (H_2)_2\end{array}\right\}N_2,$$

Tetrethylated benzidine ....
$$\left.\begin{array}{c}(C_{12}H_8)''\\ (C_2H_5)_2\\ (C_2H_5)_2\end{array}\right\}N_2.$$

Iodides of Diammoniums.

Primary	$[(C_{12}H_8)''$	H_6	$N_2]''I_2$,
Secondary ..	$[(C_{12}H_8)''$	H_4	$(C_2H_5)_2N_2]''I_2$,
Tertiary	$[(C_{12}H_8)''$	H_2	$(C_2H_5)_4N_2]''I_2$,
Quartary......	$[(C_{12}H_8)''$	$(CH_3)_2$	$(C_2H_5)_4N_2]''I_2$.

The experiments described in this note were performed in Professor Hofmann's laboratory.

On the Constitution of Oil of Cajeput.

By Maximilian Schmidl.

(From the Transactions of the Royal Society of Edinburgh, Vol. XXII., Part VI., p. 360.)

OIL OF CAJEPUT is prepared in the East Indies, by distilling the leaves of *Melaleuca Leucodendron* with water. It was formerly used to a great extent as an external and even as an internal medicine; but has now become more or less obsolete, and is seldom met with in a pure or unchanged state, except in the hands of wholesale druggists. As introduced into Europe, it possesses a light green colour, resembling that of a dilute solution of chloride of chromium, which is caused by a resinous colouring matter dissolved in it in very small quantity.

The colour of the crude oil is also partly due to copper, the presence of which may be accounted for, either by the use of a copper head in the distilling apparatus of the Indians, or by intentional adulteration resorted to for preserving the green colour of the oil, which otherwise changes gradually by oxidation to a reddish-brown, the oil then becoming unsaleable for medicinal purposes. That the oil possesses a green colour of its own, is proved by the fact that the colour remains after the complete removal of the copper by sulphuretted hydrogen.

Oil of cajeput consists mainly of the bihydrate of a hydrocarbon (*cajputene*) isomeric with oil of turpentine. Its specific gravity is 0·926 at 10° C. On submitting it to fractional distillation, bihydrate of cajputene, which constitutes about two-thirds of the crude oil, passes over between 175° and 178° C.; smaller fractions, perhaps products of decomposition, are obtained from 178° to 240° C., and from 240° to 250°, and at 250° only a small residue is left, consisting of carbonaceous and resinous matter mixed with metallic copper. On treating this residue with ether, a green solution is obtained, which, when evaporated, leaves a green resin, soluble in the portion which boils between 175° and 178° C., and capable of restoring its original colour.

CAJPUTENE, $C_{20}H_{16}$, is obtained, together with two isomeric hydrocarbons, (*isocajputene* and *paracajputene*) by cohobating bihydrate of cajputene with anhydrous phosphoric acid for half an hour, and then distilling off the liquid, whereupon cajputene passes over at 160°—165° C., isocajputene at 176°—178°, and paracajputene at 310°—316°.

Cajputene is perfectly colourless, and has a very pleasant odour resembling that of hyacinths. Sp. gr. = 0·850 at 15° C. Vapour-density by experiment 4·717; by calculation, supposing the molecule to occupy 4 volumes of vapour, it is 4·712.

Cajputene is permanent in the *air*. It is not affected by *iodine* at ordinary temperatures, but at a higher temperature, hydrogen is evolved and a black liquid is formed. *Bromine* acts quickly on it, producing a dark viscid oil. With *gaseous hydrochloric* acid, it forms a beautiful violet liquid, but no crystalline compound, even at—10° C. A mixture of ordinary *nitric* and *sulphuric acids* act upon it with violence, forming a yellow brittle resin.

Cajputene is insoluble in *alcohol*, but dissolves in *ether* and in *oil of turpentine.*

Isocajputene $C_{20}H_{16}$.—Obtained: (1.) as above. (2.) By distilling the bihydrate of cajputene with oil of vitriol. It is an oil boiling between 176° and 178° C. Its odour is less agreeable than that of cajputene, and becomes more pungent and aromatic by exposure to the air, the oil at the same time acquiring a yellow colour. Sp. gr. = 0·857 at 16° C. Vapour-density of (1) = 4·82; of (2) = 4·52.

Iodine, bromine, gaseous hydrochloric acid, and a mixture of *nitric* and *sulphuric acids*, act upon isocajputene in the same manner as on cajputene. With *oil of vitriol*, and with *dilute sulphuric, hydrochloric* or *nitric acids* (neither of which acts upon cajputene), it forms dark viscid liquids.

Isocajputene is insoluble in *water* and in *alcohol*, but mixes in all proportions with *ether* and with *oil of turpentine*.

Paracajputene $C_{40}H_{32}$.—Obtained, as above mentioned, by distilling bihydrate of cajputene with anhydrous phosphoric acid; and passes over between 310° and 316° C. It is very viscous, has a lemon-yellow colour, and in certain directions exhibits deep-blue fluorescence. Vapour-density by experiment 7·96; by calculation (4 vol.) = 9·424.

The difference between the experimental and calculated vapour-densities is probably due to decomposition, taking place at the high temperature required for the determination.

Paracajputene oxidises rapidly in contact with the *air*, acquiring a red colour and resinous consistence. A mixture of *nitric* and *sulphuric acids* does not act so violently on it as on cajputene and isocajputene. With *hydrochloric acid gas*, it forms a dark viscid liquid which does not yield crystals, even at—10° C. It is insoluble in *water, alcohol*, and *oil of turpentine;* soluble in *ether*.

HYDRATES OF CAJPUTENE.—*a*. Mono-hydrate $C_{20}H_{16}.HO$.—Obtained by the action of oil of vitriol on oil of cajeput. When the crude oil is raised to the boiling point in a deep open vessel, and oil of vitriol continuously dropped into it, violent ebullition takes place, accompanied, after a while, by a peculiar crackling sound. As soon as this is observed, the flame must be lowered and the acid very cautiously added till the liquid suddenly assumes a dark colour, extending in an instant from the surface throughout the whole depth. The vessel must then be immediately removed from the fire, otherwise further decomposition will take place, attended with evolution of sulphurous acid. The upper oily liquid is separated from the acid on which it floats, then well washed, and distilled, and the portion which passes over from the 170° to 175° is collected and rectified. It is an oily liquid, having a vapour-density of 5·19 to 5·27; by calculation (4 vol.) = 5·024.

This vapour-density is anomalous, inasmuch as the molecule $C_{20}H_{17}O$, which occupies four volumes of vapour, contains but 1 atom of oxygen. Probably the true formula of the body is

$C_{40}H_{34}O_2 = C_{40}H_{32} + H_2O_2$, this molecule splitting up at high temperatures into $C_{40}H_{32}$ and H_2O_2, each of which occupies four volumes of vapour, and consequently the two together occupy 8 volumes.*

b. Bihydrate, $C_{20}H_{18}O_2 = C_{20}H_{16}.2HO$.—This is the chief constituent of oil of cajeput, and passes over in the fractional distillation between 175° and 178° C. After rectification, it is a colourless oil which boils constantly at 175°, has a specific gravity of 0·903 at 17°, and vapour-density = 5·43; the calculated vapour-density (4 vol.) is 5·38.

When exposed to the *air* for a considerable time in the moist state, it changes to a reddish liquid which ultimately exhibits a rather strong acid reaction with litmus. *Iodine* dissolves in the oil, and under certain circumstances forms crystalline compounds (p. 69). *Bromine* acts quickly upon it, and forms crystalline compounds under similar circumstances. *Chlorine gas* passed into the oil raises the temperature, but does not appear to act upon it further; but *nascent* chlorine (evolved by passing hydrochloric acid gas into the oil mixed with dilute nitric acid) converts it into bichloride of cajputene $C_{20}H_{16}Cl_2$. *Anhydrous phosphoric acid* heated with the bihydrate, takes away the whole of its water, converting it into cajputene, isocajputene, and paracajputene (p. 64). *Chloride of zinc* likewise dehydrates it, but less completely. *Strong sulphuric acid* acts but very slowly on the oil at low temperatures; but if the temperature be allowed to rise, sulphurous acid is given off, and the oil blackens and ultimately suffers complete decomposition. If the action be checked at a certain point, a sulpho-acid is formed, which yields a soluble baryta-salt. Strong sulphuric acid dropped into the oil at the boiling heat, in the manner described at page 65, takes away half the water, forming mono-hydrate of cajputene. *Dilute sulphuric acid* on the contrary causes the bihydrate to take up 4 At. more water, converting it into $C_{20}H_{16}+6HO$. *Fuming sulphuric acid* converts the bihydrate into a thick brown liquid, which boils above 360°. *Fuming nitric acid* rapidly oxidises the oil, even at ordinary temperatures, forming a large quantity of oxalic acid. Ordinary nitric acid produces the same effect at the boiling heat, but at ordinary temperatures, it over acts very slowly, converting the oil into a red liquid. Distilled *permanganate* or *bichromate of potassium* in presence of sulphuric acid, it forms a thick resinous liquid. It does not appear to be altered by digestion with *peroxide of lead.* In contact with aqueous *potash,* or when dropped into melting potash, it forms a soluble salt, the acid of which is precipitated as a resin by hydrochloric or sulphuric acid. Heated with *sodium*, it forms a crystalline mass, soluble in water and alcohol, and consisting of soda and an organic substance, which is separated by strong acids in the form of a fragrant resin. When the vapour of the bihydrate is passed over red hot *soda-lime*, a yellow oil distils over, having a peculiar odour quite different from that of the bihydrate, and at the same time the soda-lime becomes blackened by deposited charcoal, and when treated with acids, gives off a large quantity of carbonic acid. The yellow oil thus formed yielded by distillation a fraction boiling between 180° and 185° C., which gave in two analyses, 79·76 and 80·03 p. c. C, 12·20 and 12·07 H, agreeing nearly with the formula $C_{26}H_{24}O_{26}$ which requires 79·59 p. c. C, 12·44 H, and 7·97 O.

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* See "Observations on Anomalous Vapour-densities," by Dr. Hofmann; (Proceedings of the Royal Society, vol. x, pp. 224, 596); also Gmelin's Handbook, English Edition, xiii, 487.

Bihydrate of cajputene dissolves in all proportions in *alcohol, ether*, and *oil of turpentine*.

c. Hexhydrate, $C_{20}H_{22}O_6 = C_{20}H_{16},6HO$.—Produced by the action of dilute sulphuric acid on the bihydrate, or on crude oil of cajeput. Two parts of dilute sulphuric acid are added to 1 part of the crude oil; and the mixture is well shaken for several days till the watery layer acquires a yellowish colour, and then left to itself for about ten days, whereupon it deposits crystalline tufts of the hexhydrate, adhering to the sides of the vessel.

The crystals melt at 120° C., and solidify again at 85°. On submitting them to dry distillation, an oily liquid passes over and condenses again in the colder parts of the apparatus, apparently as the unaltered hexydrate. The crystals dissolve sparingly in cold, easily in boiling alcohol.

Crystals having the same composition were deposited from a secondary fraction of crude cajeput-oil, which distilled at 216°—230° C., and was left for a very long time moist and exposed to the air. The crude oil mixed with nitric acid and alcohol, changes, in the course of seven or eight months, into a black heavy liquid in which crystals are suspended, perhaps consisting of the hexhydrate. The same compound appears likewise to be formed in beautiful long prisms, when the crystalline mass produced by passing hydrochloric acid gas into rectified oil of cajeput is thrown into water or alcohol.

CHLORIDE OF CAJPUTENE. $C_{20}H_{16}Cl_2$.—Produced by the action of nascent chlorine on the bihydrate. When the portion of cajeput oil, distilling between 175° and 178° C., is mixed with very dilute nitric acid, and hydrochloric acid gas is passed into the liquid, a violent action takes place in a few minutes, yellow and red fumes of chlorine and nitrous gas being evolved, and if the passage of the gas be continued, chloride of cajputene ultimately sinks to the bottom, as a limpid brown oil, which may be freed from adhering nitric and nitrous acid by distillation over strong potash-ley. It has a fragrant odour, and may be kept for any length of time without alteration, but is decomposed by distillation. Boiled with nitrate of silver, it detonates in a peculiar manner and forms chloride of silver.

Crystals were once obtained by keeping the oil at a low temperature, but not in sufficient quantity for analysis.

MONOHYDROCHLORATE OF CAJPUTENE. $C_{20}H_{16},HCl$.—Obtained by distilling the bihydrochlorate, and collecting apart the fraction which boils at 160°.

A product having the same composition is obtained by treating the bihydrochlorate for several days with aqueous or alcoholic potash; but its odour is different from that of the product obtained by simple distillation of the hydrochlorate, and resembles that of pelargonic ether.

BIHYDROCHLORATE OF CAJPUTENE. $C_{20}H_{16},2HCl$.—Obtained by passing hydrochloric acid gas through rectified cajeput-oil, mixed with a third of its volume of alcohol or strong aqueous hydrochloric acid. Crystallises from alcohol in beautiful radiating tufts. Melts at 55° C., and solidifies again at 30°. It has no taste or smell. By dry distillation, it gives off hydrochloric gas at 60°, and splits into several fractions, one of which is the monohydrochlorate. It is also deprived of half its chlorine by heating with aqueous or alcoholic potash. It dissolves sparingly in cold, easily in boiling alcohol or ether.

When hydrochloric acid gas is passed through rectified oil of cajeput, kept at a low temperature, a violet liquid is formed which in 10 or 15 minutes solidifies in a crystalline mass. This crystalline compound is extremely deliquescent, liquefying rapidly even when pressed between blotting paper cooled to —25° C.; the resulting liquid rapidly gives off fumes of hydrochloric acid, and is completely decomposed by distillation. If the crystalline mass, immediately after its formation, be thrown into water or alcohol, beautiful long prisms are formed, after a few days, apparently consisting of hexhydrate of cajputene.

BROMIDE OF CAJPUTENE. $C_{20}H_{16}Br_4$.—Obtained by the action of bromine on oil of cajeput. When dry bromine is dropped into the rectified oil, a very brisk action takes place, and the sides of the vessel become covered with yellow needles, which however soon disappear; but if the addition of the bromide be continued till the reaction almost ceases, a dark, thick, viscous oil is formed, which, after several weeks, deposits a granular substance. By boiling the mixture with alcohol, the granular substance is extracted; a heavy oil is left behind; and the alcoholic solution, on cooling, deposits bromide of cajputene as a soft crystalline substance, having a fatty lustre and much resembling cholesterin.

Bromide of cajputene melts at 60° C, and solidifies again at 32°.

By dry distillation, it yields a liquid which crystallises again in the cooler parts of the retort. It is not altered by boiling with aqueous potash. It dissolves in ether and in boiling alcohol.

Rectified oil of cajeput shaken up with bromine-water forms a red resin, from which a solid substance separates in small white prisms, extremely deliquescent and rapidly decomposing.

Another crystallised bromine-compound (probably a hydrobromate analogous to the hydriodate), is formed in the same manner as that compound.

Hydriodate of Cajputene.—*a. Anhydrous,* $C_{20}H_{16},HI$.—Obtained by adding a solution of phosphorus in bisulphide of carbon to a solution of iodine and oil of cajeput in the same liquid. Brisk action then takes place, the vessel becoming very hot; red oxide of phosphorus is precipitated; the oily liquid becomes reddish; and gives off vapours probably containing phosphurretted hydrogen, and if left to itself for 10 or 12 days, deposits crystals of the hydriodate. The reaction probably takes place as represented by the equation:

$$3C_{20}H_{16} + 3PI + 6HO = 3C_{20}H_{17}I + PH_3 + PO + PO_5$$

The crystals of the hydriodate are deposited in cells like those of beehives, and possess a black metallic lustre. They are soluble in alcohol and in ether, and are very stable, not being altered, even by boiling with potash.

b. *Hydrated,* $C_{20}H_{18}IO = C_{20}H_{16}HI + HO$., or *Hydriodate of Monohydrate of Cajputene*. $C_{20}H_{17}O,HI$.—When iodine is added in small quantities to cajeput oil, crude or rectified, at ordinary temperatures, no visible action takes place (if external heat be applied, the action goes too far and nothing but a viscous mass is produced which does not crystallise); but on stirring rather constantly, the action is assisted, partly by the heat resulting from the friction of the glass rod, partly by the mechanical distribution of the iodine, and the temperature of the liquid soon rises from 10° to 40° C. The addition of iodine must then be discontinued, and the vessel immersed in cold water. A black crystalline compound then separates after a short time; and on separating this substance from the oily liquid by filtration, pressing it between blotting paper, and when it is nearly dry, dissolving it in alcohol or ether, a solution is obtained, from which the hydrated hydriodate crystallises in prisms having a fine yellow-green colour and metallic lustre. They are very deliquescent, and melt at 80° C. into a liquid which does not recrystallise in the cold. Potash-ley liquefies the compound, abstracting part of the iodine, and with the aid of heat abstracts the whole.

It is insoluble in *water,* and is not decomposed thereby; very soluble in *alcohol* and *ether*.

On the Basic Carbonates of Copper.

By Frederick Field.

On adding sulphate of copper to a great excess of solution of sesquicarbonate of soda, no precipitate is obtained until a considerable quantity of the copper-salt has been introduced. Even then, on gently warming, the small precipitate of carbonate of copper is dissolved, forming a bright blue solution. When this liquid is boiled for some time, a green granular precipitate is obtained, the supernatant liquid still holding copper in solution with great tenacity, and maintaining its clear blue colour. If the ebullition has not been continued for more than half an hour, on filtering the liquid from the precipitate, the former is found to be capable of dissolving a further quantity of copper, which is precipitated as a green powder similar to the last. After very protracted ebullition, however, the filtrate from this last precipitate yields, on the introduction of sulphate of copper, not a green powder, but one of a dense black colour.

Composition of the Green Precipitate.—After thorough washing, the green compound was dried on a water-bath until it ceased to lose weight, and the copper and carbonic acid were determined, the water being estimated as loss.

	I.	II.
Copper	57·46	57·21
Carbonic acid	19·45	19·31

This compound is identical in composition with the ordinary green dicarbonate and malachite, as shown by the following numbers, which, for the sake of comparison, are placed in juxtaposition with the results obtained in the analysis of a fine specimen of pure malachite from the west coast of Africa, and some beautiful crystals of native dicarbonate of copper from Chili.

	Green Precipitate.	Malachite.	Crystals.	Calculated.
CuO	71·81	71·74	71·69	72·06
CO_2	19·45	19·68	19·80	19·82
HO (loss)	8·74	8·58	8·51	8·12
	100·00	100·00	100·00	100·00

Composition of the Black Precipitate.—This compound, after boiling with the strongly alkaline liquid for a considerable time, was washed and dried in a water-bath.

On analysis, it was found to consist of 4 equivalents of oxide combined with one of dicarbonate of copper, or, which is the same thing, 6 of oxide of copper and 1 of carbonic acid, as the following numbers will show:

	Found.		Calculated.
	I.	II.	
CuO	91·42	91·39	91·60
CO_2	8·44	8·51	8·40

Very long protracted boiling of the alkaline liquid was necessary to convert this compound into oxide of copper. Suspended in pure boiling water, it is decomposed in a few minutes.

When powdered malachite is introduced into boiling water, the mineral blackens in a few minutes, and after half an hour's brisk ebullition, is entirely converted into black oxide. Artificially prepared dicarbonate suffers the same reaction. When equivalent proportions of sulphate of copper and carbonate of soda are dissolved in water, the ultimate result is the same, although much retarded by the sulphate of soda in solution. I could obtain no decomposition of either the mineral or the artificial compound in a boiling solution of chloride of sodium.

When sulphate of copper is gradually added to a strong solution of carbonate of soda an immediate blue precipitate occurs, on the addition of the first few drops, unaccompanied by effervesence, and by the further introduction of the copper-salt, no more precipitation takes place, but a dark blue solution is formed. When this is heated, it immediately darkens, owing to the formation of a black powder. The addition of sulphate of copper to the supernatant carbonate of soda causes a bright temporary blue colour which is almost instantaneously changed into the black. Washed and dried this substance was found to contain:

	I.	II.
CuO	91·49	91·52
CO	8·38	8·41

and thus to have the same composition as the one mentioned above, viz.: $4CuO,2CuO,CO_2$. This highly basic carbonate can be boiled with carbonate of soda for many hours without decomposition; suspended in pure boiling water it is speedily decomposed.

Action of Carbonate of Soda upon Dicarbonate of Copper. When a solution of carbonate of soda is heated, even only to the temperature of 120°F, and powdered malachite or artificial dicarbonate is introduced, decomposition quickly takes place, as is shown by the darkening of the compounds. An evolution of carbonic acid always accompanies the reaction. A few minutes boiling yields the compound $4CuO, 2CuO,CO_2$.

It may further be remarked that when dicarbonate of copper either artificially prepared or as malachite, is boiled with a solution of sesquicarbonate of soda, it is dissolved and a blue solution is formed which is not decomposed, after long ebullition, sesquicarbonate of soda containing carbonate of copper in solution appearing to resist the action of heat far more strongly than it does in the absence of the latter metal.

When sulphate of copper is added to a mixed solution of a sesquicarbonate and sulphite of soda, no precipitate is formed. An easy and safe method of de-oxidation consists in adding a mixture of about equal parts of sesquicarbonate and sulphite of soda to a hot solution of a proto-salt of copper. After heating for some little time, the introduction of a slight excess of hydrochloric acid produces a solution which is perfectly colourless, and gives with potash the clear orange precipitate of the suboxide, and with ammonia no blue shade if the air be carefully excluded. With regard to the precipitation of copper from its various salts, as protoxide, it is much better to employ hypochlorite of soda, than caustic potash. The precipitate subsides more quickly, and is infinitely easier to wash.

Contributions to the History of the Phosphorus Bases.

By Augustus William Hofmann, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

SECOND MEMOIR.

Theory of Diatomic Bases. Diphosphonium-Compounds.

In surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot avoid recognizing as one of the most valuable amongst these acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the classical researches of Graham and Liebig on the polybasic acids, and afterwards extended and generalized by the experiments of Gerhardt and Williamson, it has acquired in Berthelot's beautiful investigation of glycerin, a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. Buff, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation, until, in the brilliant experimental researches of Wurtz, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination.

Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained. For, as from a single molecule of water, a monatomic alcohol, a monobasic acid, or a monacid base can be produced, according to the nature of the monatomic radical by which the hydrogen is replaced, so likewise must it be possible, by a proper selection of polyatomic radicals to link two or more molecules of water, so as to form one molecule of a polyacid base, just as the introduction of other polyatomic radicals gives rise to the formation of polyatomic alcohols or polybasic acids. It remained only to submit these ideas to the test of experiment.

Material for building up this group of bodies appeared to present itself unmistakeably in the chlorine-, bromine-, and iodine-compounds of ethylene and its homologues. Having succeeded some years ago in converting the corresponding ethyl-compounds by the action of ammonia into the monacid ethyl-bases, I was justified in expecting that by treating the ethylene-compounds with ammonia, diacid bases might be formed. Respecting some of the bodies which are produced in these reactions, investigations had already been published by Cloëz,* and more recently by Natanson,† whose results appeared at first sight to give but little encouragement to any such attempt. But a careful examination of these researches soon convinced me that, at the time when they were undertaken, chemical knowledge had not sufficiently advanced to afford a correct interpretation of the results elicited.

I have once more studied these reactions, and have obtained experimental confirmation of the correctness of my anticipations. But the action of ammonia on the chloride, bromide, and iodide of ethylene presents unexpected complications, quite independent of those indicated by theory, and for which I was not altogether prepared.

Consider for a moment the manner in which the reaction between ammonia and a diatomic bromide—dibromide of ethylene for instance—may take place. Just as bromide of ethyl, acting, as it does, on a single molecule of ammonia, gives rise to the formation of the four bromides,

$$\begin{array}{r} [(C_2H_5)\ H_3N]Br,‡ \\ [(C_2H_5)_2H_2N]Br, \\ [(C_2H_5)_3H\ \ N]Br, \\ \text{and } [(C_2H_5)_4\ \ \ \ N]Br, \end{array}$$

so likewise may dibromide of ethylene, acting on two molecules of ammonia, be expected to produce four diatomic bromides, viz.—

$$\begin{array}{r} [(C_2H_4)''\ H_6N_2]''Br_2, \\ [(C_2H_4)_2''H_4N_2]''Br_2, \\ [(C_2H_4)_3''H_2N_2]''Br_2, \\ \text{and } [(C_2H_4)_4''\ \ \ \ N_2]''Br_2. \end{array}$$

These, however, are by no means the only compounds which, in accordance with our present conception of diatomic compounds, may be formed in this reaction.

It appears from the researches of Wurtz, that dibromide of ethylene does not pass into ethylene-alcohol at a single bound, but that there exists an intermediate member of the series still containing half the bromine.

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* Instit. 1853, p 213. † Ann. Ch. Pharm. xcii. 48, and xcviii. 291.

‡ H=1; O=16; S=32; C=12, &c.

$(C_2H_4)''\left\{\begin{matrix}Br\\Br\end{matrix}\right.$	$(C_2H_4)''\left\{\begin{matrix}Br\\HO\end{matrix}\right.$	$(C_2H_4)''\left\{\begin{matrix}HO\\HO\end{matrix}\right.$
Dibromide of Ethylene.	Intermediate Bromide.	Ethylene-alcohol.

There could, therefore, be no doubt that dibromide of ethylene would, under certain conditions, likewise react with ammonia as a monatomic compound, giving rise to another series of bodies in which the hydrogen would be more or less replaced by the monatomic radical C_2H_4Br, viz.—

$$\begin{array}{rl} & [(C_2H_4Br)\ H_3N]Br, \\ & [(C_2H_4Br)_2H_2N]Br, \\ & [(C_2H_4Br)_3H\ N]Br, \\ \text{and} & [(C_2H_4Br)_4\quad N]Br. \end{array}$$

Further, if the reaction took place in presence of water, it was to be expected that the bromine, wholly or partially eliminated as hydrobromic acid, would be replaced by the molecular residue of the water; and thus, independently of any mixed compounds containing bromine *and* oxygen, a series of salts might be looked for, in which a molecule $C_2H_4HO=C_2H_5O$ would enter monatomically, viz.—

$$\begin{array}{rl} & [(C_2H_5O)\ H_3N]Br, \\ & [(C_2H_5O)_2H_2N]Br, \\ & [(C_2H_5O)_3H\ N]Br, \\ \text{and} & [(C_2H_5O)_4\quad N]Br. \end{array}$$

Lastly, remembering the tendency exhibited by ethylene-compounds to resolve themselves, in presence of alkalies, into vinyl-compounds, it appeared not improbable that a fourth series of bodies would likewise be formed, viz.—

$$\begin{array}{rl} & [(C_2H_3)\ H_3N]Br, \\ & [(C_2H_3)_2H_2N]Br, \\ & [(C_2H_3)_3H\ N]Br, \\ \text{and} & [(C_2H_3)_4\quad N]Br; \end{array}$$

and thus was presented the not very inviting problem of separating from a great mass of bromide of ammonium, no fewer than sixteen different bases.

In the experiments on the action of dibromide of ethylene on ammonia and its homologues, which I intend to publish in a special paper, I have indeed by no means met with the whole of these compounds; but in place of the deficient members of the groups, new products have made their appearance, whose formation in the present state of our knowledge could scarcely have been predicted. Without entering into details respecting these products, I will merely observe that I was induced, by the complication of this reaction, to subject dibromide of ethylene to the action of ethylamine, diethylamine, and finally of triethylamine instead of ammonia; for it could not be doubted that with the progressive substitution of ethyl for the hydrogen in ammonia, the process would be simplified, the number of possible products of reaction being considerably diminished. Ammonia indeed—omitting secondary products—is capable of producing not less than *sixteen* compounds, whereas ethylamine cannot yield more than *twelve*, diethylamine not more than *eight*, and in the reaction between triethylamine and dibromide of ethylene, the number of compounds possible under the most favourable circumstances is limited to *four*. Experiment has verified this anticipation; in the same proportion as the substitution advances in the ammonia submitted to the action, the number of products generated diminishes; nevertheless the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus-series, using, instead of triethylamine, the corresponding phosphorus-base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory, undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness; and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality, such as I have never observed in any similar reaction among bodies of the nitrogen-series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus-series.

ETHYLENE-GROUP.

Action of Dibromide of Ethylene on Triethylphosphine.

When these two bodies are brought together in quantities not too large, the liquid becomes turbid, but no rise of temperature takes place to indicate the occurrence of chemical action. The mixture, after being left to itself for a few hours, deposits white crystals, the formation of which continues till the entire liquid is converted into a white saline mass. If the mixture be even gently heated, the crystallization takes place instantaneously, and a violent reaction sets in, which is very apt to project a portion of the resulting salt from the vessel. In operating on rather a large scale in vessels filled with air, the heat evolved on agitation, in consequence of the oxidation of the phosphorous-base, is often sufficient to start the reaction.

In preparing considerable quantities of the white crystals, I have therefore found it convenient to add to the triethylphosphine twice its volume of ether, to mix the ethereal solution with the dibromide of ethylene in a flask filled with carbonic acid gas, and to heat the mixture in a water-bath, the flask being provided with an inverted cooling apparatus, so that the vapours which escape may be condensed and returned. Or, the mixture of triethylphosphine, dibromide of ethylene and ether may be introduced into long tubes previously drawn out, and the tubes, after sealing, immersed for some hours in boiling water. As the value of dibromide of ethylene is trifling in comparison with that of triethylphosphine, I always, in commencing the study of this reaction, used the former substance in excess. The triethylphosphine is quickly fixed by the dibromide of ethylene, and the action may be considered as terminated when the presence of the free phosphorus-base in the mixture is no longer indicated by disulphide of carbon. As soon as this point is attained, the crystalline bromides may be thrown on a filter, the ether allowed to drain off, and the crystals freed from excess of bromide of ethylene by washing them for a while with anhydrous ether, in which they are quite insoluble.

The crystals thus obtained dissolve with great facility in water and in ordinary alcohol, somewhat less readily in boiling absolute alcohol. This solution on cooling deposits well-developed crystals, which sustain a heat of 100°C without decomposition, but show a slight tendency to deliquesce in the air. The analysis of these crystals, and their behaviour with reagents, showed unmistakeably that, in the action of dibromide of ethylene on triethylphosphine, at least two bromides are formed. The determination of the bromine by means of nitrate of silver in the products of different preparations, purified by successive crystallizations from alcohol, gave percentages of bromine varying from 32·1 to 25·94. On again repeating the crystallization, the amount of bromine precipitated by nitrate of silver did not exhibit any further diminution.

The complete analysis of the crystals, purified by a great number of crystallizations from alcohol, has led me to the simple expression

$$C_8H_{19}PBr_2=C_6H_{15}P+C_2H_4Br_2,$$

whence it appears that the body is produced by the combination of one molecule of triethylphosphine with one molecule of the bromine-compound.

The purification of the second substance, yielding with nitrate of silver a larger proportion of bromine, which remains in the mother-liquor of the compound just described, is somewhat complicated. As I shall have to return to this body in the description of the individual compounds, I content myself in this place with just setting forth the general character of the reaction by quoting the formula deduced from its examination. The analysis of this bromine-compound, together with those of a whole series of bodies derived from it, has led to the formula

$$C_{14}H_{34}P_2Br_2 = 2C_6H_{15}P + C_2H_4Br_2,$$

showing that the body is a compound of two molecules of triethylphosphine and one molecule of dibromide of ethylene.

These observations are sufficient to establish the peculiar nature of the reaction in question. There are clearly two successive phases to be distinguished, according as the bromide of ethylene lays hold of one or two molecules of triethylphosphine; secondary products may likewise be formed, which for the present may be left out of consideration, as I shall have to allude to them in the course of the memoir. It is, however, worth while to mention in this place that, when the experiment is made with pure substances, and under the conditions above mentioned, the two bromides described are almost the only products of the reaction.

These two bodies have become the starting-points of two extensive groups of compounds, which may even now be distinguished as the *series of monatomic compounds*, and the *series of diatomic compounds*.

I now proceed to the detailed description of the individual members of these series.

SERIES OF MONATOMIC COMPOUNDS. MONOPHOSPHONIUM-COMPOUNDS.

Salts of Bromethyl-triethylphosphonium.

Bromide of Bromethyl-triethylphosphonium.—By this long name I designate the crystalline substance which is produced by the union of one molecule of dibromide of ethylene and one molecule of triethylphosphine. The preparation of this compound has already been given in the preceding paragraph. It is the chief product of the reaction when the dibromide of ethylene is in excess.

The equation

$$C_2H_4Br_2 + C_6H_{15}P = C_8H_{19}PBr_2$$

requires about 1 vol. of dibromide of ethylene to 1·5 vol. of triethylphosphine; but even when a larger quantity of the bromine-compound is *heated* with the phosphorus-base, either in presence or absence of ether or alcohol, we always obtain an appreciable quantity of the second bromide. It is only by allowing an *immense* excess of dibromide to act at the *common temperature* upon triethylphosphine, either in presence or absence of ether, that the formation of the second bromide is altogether avoided. In this reaction, which is not complete in less than twenty-four hours, a considerable quantity of gas is evolved, which does *not* appear when the substances are heated together.

To purify the product, which contains appreciable quantities of the second bromide, it is necessary to crystallize it at least three or four times from absolute alcohol; in the last crystallization it is desirable to mix the alcoholic solution with a moderate quantity of ether. The solution, if left to itself, frequently deposits separate well-defined crystals, which may be dried without decomposition at 100°, and which melt at about 235° C with partial decomposition, hydrobromic acid being abundantly evolved.

A simple experiment showed that nitrate of silver precipitates from this compound only part of the bromine. When the liquid filtered from the precipitated bromide of silver was mixed with carbonate of sodium, to remove the excess of silver, and evaporated, the residue, when ignited with lime and dissolved in nitric acid, gave, on addition of nitrate of silver, a fresh quantity of bromide of silver. I therefore endeavoured to obtain the entire quantity of bromine by means of recently precipitated oxide of silver, a process which I had previously found serviceable in similar cases. The result confirmed my anticipation. Digestion with oxide of silver removes the whole of the bromine, and shows that the quantity precipitated by nitrate of silver is only half the total amount.

The analysis* of this substance led to the formula, already quoted,

$$C_8\,H_{19}P\,Br_2,\dagger$$

the interpretation of which presents no difficulty. The crystals are evidently the bromide of a monophosphonium in which 3 eqs. of ethyl are substituted for 3 equivs. of hydrogen, the last equivalent of hydrogen being replaced by a secondary radical, C_2H_4Br, which for the present I will call *monobrominated ethyl* or *bromethyl.*

The molecular formula

$$[(C_2H_4Br)\ (C_2H_5)_3P]\ Br$$

represents the constitution of this salt.

I have already observed that this bromide is occasionally obtained in well-defined crystals. They were examined by Quintino Sella:

" System monometric (regular).

The crystals exhibit the form of the rhombic dodecahedron 110 (Fig. 28).‡ They are sometimes elongated so as to present the aspect of dimetric crystals, as in Fig. 29. Sometimes it even happens that one of the faces $\bar{1}\ 1\ 0$ is much more developed than the parallel face $1\ \bar{1}\ 0$ (Fig. 30), so that scarcely more than half the crystal (Fig. 29) appears to exist. Sometimes the faces exhibit striæ parallel to the adjacent edges of the rhombic dodecahedron.

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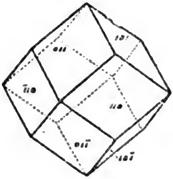
* The details of the analytical determination are given in the original papers published in the Philosophical Transactions for 1860.

† H = 1; O = 16; S = 32; C = 12.

‡ The figures are numbered consecutively, with that in Dr. Hofmann's former paper on the phosphorus bases, vol. xiii, p. 289, of this Journal.

Fig. 28.



Feb. 29.

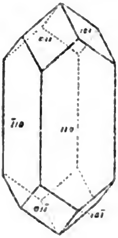
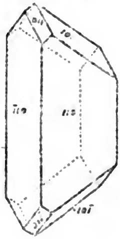


Fig. 30.



Lustre fatty.

Hardness inferior to that of gypsum.

The crystals have no action on polarized light."

By treating the bromide with silver-salts *in the cold*, the bromine external to the phosphonium-metal is replaced by the acid-radical united with the silver, while the bromine belonging to the phosphonium remains untouched. In this manner, we obtain the salts of the new metal, which exhibit an inclination to unite with excess of the silver-salts, in the form of double compounds. The *chloride* and the *nitrate* prepared from the bromide by the action of chloride and nitrate of silver are extremely soluble in water and alcohol, and crystallize indistinctly. The *sulphate* forms long white crystalline needles, likewise very soluble in water and alcohol. It is very easily obtained by the action of sulphuretted hydrogen on the double salt which is formed by treating the bromide with sulphate of silver; on adding alcohol and ether to the concentrated liquid containing free sulphuric acid, it is precipitated in crystals. The sulphate, treated with iodide of barium, yields the *iodide*, a salt which dissolves sparingly in water, and crystallizes in scales of a pearly lustre.

I have not examined these salts more particularly, as they scarcely present any theoretical interest, and as the composition of the bromide, which forms the starting-point of the series, is sufficiently corroborated by the analysis of the platinum- and gold-salts.

Platinum-salt.—The chloride obtained by digesting the bromide with excess of chloride of silver is mixed with dichloride of platinum, when the platinum-salt is deposited on cooling in light orange-yellow prisms, frequently an inch in length. This salt is somewhat sparingly soluble in cold, more readily in boiling water, and may be crystallized without decomposition. During the recrystallizations, this salt, under circumstances not yet clearly made out, is occasionally obtained in crystals of an octahedral habitus.

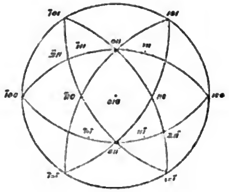
This platinum-salt, though somewhat sparingly soluble, is nevertheless essentially different from the platinum-salt of the diphosphonium to be described hereafter, which accompanies the bromethyltriethyl-phosphonium. The latter is nearly insoluble in water, and is precipitated from the most dilute solutions. This character forms a means of testing the purity of the monophosphonium-bromide in the succession of crystallizations to which it has to be submitted for the sake of purification. The salt is pure when the dilute solution after being treated with chloride of silver, no longer gives a precipitate with dichloride of platinum.

The platinum salt contains :—

$$C_8H_{19}Br\ P\ Pt\ Cl_3 = [(C_2H_4Br)\ [(C_2H_5)_3P]\ Cl,\ Pt\ Cl_2.$$

The crystalline form was likewise determined by Quintino Sella.

Fig. 31.



" System monoclinic :—

100, 101 = 55° 59′; 001, 101, = 33° 3′; 010, 111 = 60° 37′.

Forms observed:—

100, 010, 110, 101, $\bar{1}01$, 011, 111, $\bar{1}11$, $\bar{2}11$ (Fig. 31).

Fig. 32.

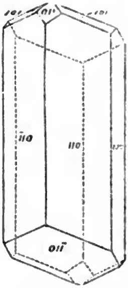


Fig. 33.

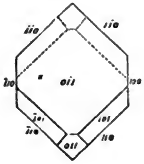
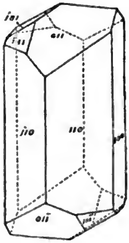


Fig. 34.



Combinations observed :—

110, 011, 100; 101, $\bar{1}01$ (Figs. 32, 33).
110, 011; 100, $\bar{1}11$, $\bar{1}01$ (Fig. 34).
110, 011; 100, $\bar{1}11$, $\bar{1}01$, $\bar{2}11$ (Fig. 35).
110, $\bar{1}11$; 100, $\bar{1}01$, 011, 111 (Fig. 36).
110, 011, 100, 111; 101, $\bar{1}11$, $\bar{2}11$ (Fig. 37).
110, 011, 100; 010, 011, $\bar{1}01$, 211 (Figs. 38, 39).

Fig. 35.

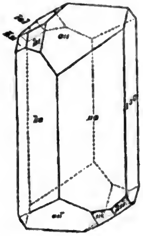
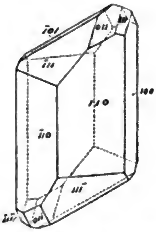


Fig. 36.



The faces 0 1 1 are often very irregularly developed, as seen in Figs. 32, 33, and 38, 39; under these circumstances some of the faces of the forms 1 1 1, $\bar{1}\,1\,1$, $\bar{2}\,1\,1$ are apt to disappear, as may be seen in Figs. 38 and 39.

Fig. 37.

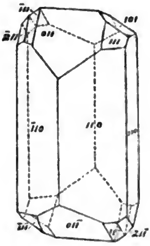


Fig. 38.

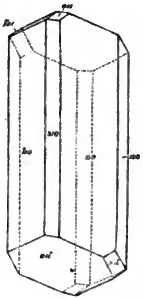
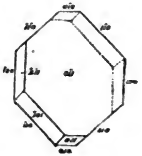


Fig. 39.



Cleavages: 1 0 0, 1 1 0.

Colour: orange with a tint of yellow in minute, and of red in larger, crystals.

The plane of the optical axes is parallel to the axis of symmetry [0 1 0]: for rings are observed across the faces of the prism 1 1 0 symmetrically with [0 1 0]."

Gold-salt.—Light yellow needles, difficultly soluble in cold water, recrystallizable from boiling water, containing

$$C_8H_{19}Br\,P\,Au\,Cl_4 = [(C_2H_4Br)\,(C_2H_5)_3P]\,Cl_3,\ Au\,Cl_3.$$

I have in vain endeavoured to prepare the hydrate

$$C_8\,H_{20}\,Br\,P\,O = \left.\begin{matrix}[(C_2\,H_4\,Br)\,(C_2\,H_5)_3\,P]\\ H\end{matrix}\right\}O$$

belonging to these salts.

In quoting the analysis of the bromide, I have already mentioned that this salt, when treated with oxide of silver, gives up the whole of its bromine. On mixing the caustic liquid filtered from the silver-salt with hydrochloric acid and dichloride of platinum, we no longer obtain the sparingly soluble platinum-double salt crystallizing in the characteristic needles; but the liquid, after being considerably concentrated by evaporation, yields well-defined, reddish-yellow octahedra belonging to another base. An exactly similar result is obtained on attempting to separate the base from the sulphate by means of baryta. After filtering off the sulphate of barium, there remains a strongly alkaline liquid, which likewise yields only the octahedral platinum-salt, while the presence of bromide of barium in the solution indicates the transformation of the original molecular system. The elimination of the second equivalent of bromine by silver-salts, which takes place instantly and completely in alkaline liquids, may likewise be effected by continual ebullition in neutral and even in acid solutions, though always slowly and incompletely. If the bromide be precipitated by excess of nitrate of silver, the filtered liquid, on being boiled and evaporated, deposits a fresh quantity of bromide of silver; but in most cases, even after long-continued boiling, a considerable quantity of bromine remains latent, and may be immediately recognized by again filtering the liquid and slightly supersaturating it with ammonia, the whole of the remaining bromine being then precipitated as bromide of silver. This deportment furnishes in fact a characteristic distinction of the bromethylated bromide, by which this substance may often be conveniently recognized. It deserves to be remarked that the fixed caustic alkalies exert but a slight action on the bromethylated bromide; the compound is precipitated by the alkalies from its cold aqueous solution in the crystalline state and without decomposition, and it is only after some time that alterations take place, probably affecting its intimate constitution. The nature of these alterations has not yet been made out. The crystals may be boiled for some time with alcoholic solution of potassa without decomposition. The bromide likewise suffers no alteration by continued digestion with water or alcohol at 100°.

SALTS OF OXETHYL-TRIETHYLPHOSPHONIUM.

Iodide.—When the caustic liquid produced by treating the bromide of bromethyl-triethylphosphonium with oxide of silver is neutralized with hydriodic acid and the solution evaporated, an iodide is obtained which crystallizes in needles, and dissolves very readily in water and alcohol. The finest crystals are obtained by mixing the alcoholic solution with ether till it becomes opalescent, and then allowing it to crystallize. If too much ether has been added, the new iodide is precipitated as an oil, which solidifies but slowly to a crystalline mass. The salt becomes coloured at 100°, and must therefore be dried for analysis *in vacuo*. It was found to contain :—

$$C_8H_{20}OPI = [(C_2H_5O)]\ (C_2H_5)_3P]I.$$

The transformation of the bromethylated phosphonium takes place, therefore, exactly as might be expected from analogy, the bromine being eliminated as bromide of silver, and its place being taken by the molecular residue of the water :—

$$[(C_2H_4Br)\ (C_2H_5)_3P]Br + Ag_2O + H_2O = 2AgBr + \left.\begin{array}{r}[(C_2H_5O)\ (C_2H_5)_3P]\\ H\end{array}\right\}O.$$

Hydrate.—The caustic solution of the oxide exhibits the usual characteristic properties of this class of bodies. Over sulphuric acid, the solution thickens to a syrupy, extremely deliquescent mass, from which the base separates in oily drops on addition of potassa. Its decomposition by heat is characteristic; at a rather high temperature, it is resolved into oxide of triethylphosphine, ethylene, and water :—

$$\left.\begin{array}{r}[(C_2H_5O)\ (C_2H_5)_3P]\\ H\end{array}\right\}O = (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The oxide of triethylphosphine was identified by the preparation of its platinum-salt; the ethylene, by converting it into the bromide.

The above equation represents the final result of the action of heat; this final result, however, is preceded by several intermediate changes, to which I shall return in a subsequent section of this paper.

Bromide.—Extremely soluble. Dries up over sulphuric acid to an indistinct crystalline mass.

Chloride.—This compound resembles the bromide in every respect. Both these salts readily form double compounds with iodide and bromide of zinc. The chloride, under the influence of pentabromide and pentachloride of phosphorus, undergoes remarkable transformations, to which I shall presently recur.

Perchlorate.—Laminæ somewhat sparingly soluble in cold water.

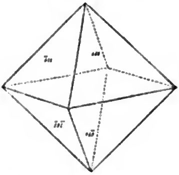
I have not analysed any of these salts, inasmuch as the composition of this series of compounds is, moreover, sufficiently established by the analysis of the platinum- and gold-salt.

Platinum-salt.—The alkaline solution, from which the iodide was obtained, yields, when saturated with hydrochloric acid, mixed with dichloride of platinum, and evaporated, the above-mentioned platinum salt, containing—

$$C_8H_{20}OPPtCl_3 = [(C_2H_5O)\ (C_2H_5)_3P]Cl,\ PtCl_2.$$

This salt is easily soluble in boiling water, and may be recrystallized without decomposition. It forms splendid octahedra, which were measured by Quintino Sella:

Fig. 40.



" System monometric :—

Form observed :—

111 (Fig. 40.)

No sensible influence on polarized light. Colour orange."

Gold-salt.—Golden-yellow needles, sparingly soluble in cold, readily in boiling water: in a quantity of boiling water not sufficient to dissolve them, they fuse to a transparent yellow oil. Not decomposed by recrystillization. Precipitated by trichloride of gold from a moderately concentrated solution of the chloride. Analysis led to the formula :

$$C_8 H_{20} O P Au Cl_4 = [(C_2 H_5 O) (C_2 H_5)_3 P] Cl, Au Cl_3.$$

I have already alluded to the decomposition which the chloride of the oxethylated phosphonium undergoes under the influence of pentabromide of phosphorus. The two bodies act upon one another with great violence: oxybromide of phosphorus and hydrobromic acid are evolved, and the residue is found to contain the chloride of the bromethylated phosphonium from which the oxethylated compound was originally produced.

$$[(C_2H_5O) (C_2H_5)_3P]Cl + PBr_5 = POBr_3 + HBr) + [(C_2H_4Br) (C_2H_5)_3P]Cl.$$

Nothing is easier than to obtain experimental proof of this transformation, which is of considerable theoretical interest. After the oxybromide and the excess of pentabromide have been removed as completely as possible by evaporation, the remaining liquid yields, on addition of dichloride of platinum, a sparingly soluble, still impure platinum-salt, which, after washing, may be decomposed by sulphuretted hydrogen and thereby purified. If the chloride thus formed be precipitated with excess of nitrate of silver, and the nitrate of the base, filtered from the chloride of silver, be mixed with ammonia and gently heated, a copious precipitate is immediately formed, consisting of bromide of silver. This reaction is characteristic of the bromethylated body. Moreover, on mixing the solution of the nitrate freed from silver with dichloride of platinum, and recrystallizing the platinum-precipitate from boiling water, the liquid yields on cooling the splendid needles of the platinum-salt of the bromethylated triethylphosphonium. The analysis of this salt was omitted, partly because no doubt could be entertained respecting its nature, and partly because I had occasion to establish by a number—as will be noticed hereafter—the nature of the precisely similar reaction between chloride of oxethyl-triethylphosphonium and pentachloride of phosphorus.

Thus it is seen that the molecular group C_2H_5O, which is supposed to replace the hydrogen in the salt, suffers, under the influence of pentabromide of phosphorus, alterations exactly similar to those which it would have undergone under similar circumstances when conceived as a constituent of alcohol.

If we consider the facility with which the bromethylated phosphonium is converted into the oxethylated compound by the action of oxide of silver, and the simple re-formation of the first-mentioned body by means of pentabromide of phosphorus, a great variety of new experiments suggest themselves. In reviewing the relations which obtain between the bromethylated and oxethylated phosphoniums, who could fail to perceive that the two hydrogen-replacing radicals, which constitute the difference between these two organic metals, stand to one another in the same relation as bromide of ethyl and alcohol, or bromide of acetyl and acetic acid? But if this be so, what a number of new bodies does this consideration bring into view, even if we limit our calculation to the transformations of which the molecular group C_2H_5O in alcohol is susceptible! As yet I have scarcely penetrated into this new field of inquiry, and I must be satisfied to quote a single experiment, which exhibits the above-mentioned bodies in a new light.

The salts of bromethylated and oxethylated triethylphosphonium may be regarded as tetrethylphosphonium salts, in which an atom of hydrogen is replaced by bromine and the radical H O respectively:

Bromide of:

Tetrethylphosphonium . . .	$[(C_2H_4H)\ (C_2H_5)_3P]Br$,
Bromethylated triethylphosphonium	$[(C_2H_4Br)\ (C_2H_5)_3P]Br$,
Oxethylated triethylphosphonium .	$[(C_2H_4HO)\ (C_2H_5)_3P]Br$,

and the question arose whether the bromethylated salt might not be converted by a simple process into the tetrethylphosphonium-compound. This transformation may indeed be effected without the slighest difficulty. On acidulating the solution of the bromethylated bromide with sulphuric acid, and digesting it with granulated zinc, the bromine is eliminated in the form of hydrobromic acid, its place being filled up by one equivalent of hydrogen:

$$[(C_2H_4Br)\ (C_2H_5)_3P]Br + 2H = HBr + [(C_2H_5)_4P]Br.$$

By decanting the liquid from the excess of zinc and treating it with oxide of silver, oxide of zinc, bromine and sulphuric acid are removed, and a solution of oxide of tetrethylphosphonium is obtained, which, when mixed with hydrochloric acid and dichloride of platinum, yields well-developed octahedra of the platinum-salt of tetrethylphosphonium.

The chloride obtained in the analysis was converted, by successive treatment with oxide of silver and hydriodic acid, into the corresponding iodide. This characteristic salt appeared on careful comparison exactly similar to the iodide of tetrethylphosphonium prepared in the ordinary way.

Here, then, we have an instance of the direct reproduction of an ethyl-compound from a body of the ethylene-group by a simple process of reduction. Similar transformations would doubtless succeed in many other cases, and this is perhaps a fitting opportunity of directing attention to the interest which the employment of this reaction would have in connection with the intermediate hydrochloric glycol-ether discovered by Wurtz. Probably this compound, when subjected to the action of nascent hydrogen, would be directly converted into alcohol:

$$(C_2H_4)'' \left\{ \begin{matrix} HO \\ Cl \end{matrix} \right. = C_2H_5ClO,$$

$$(C_2H_4)'' \left\{ \begin{matrix} HO \\ H \end{matrix} \right. = C_2H_6O\,;$$

and when considered with reference to this decomposition, would appear as monochlorinated alcohol.

It was chiefly the facility with which a tetrethylphosphonium-compound may be obtained from the bromethylated bromide that induced me to designate the hydrogen-replacing molecules C_2H_4Br and C_2H_5O, which we meet with in the compounds above described, as *bromethyl* and *oxethyl.* I was anxious to submit the ideas which guided me in the selection of these terms to the test of experiment. We know from the experiments of Regnault, that dichloride of ethylene and monochlorinated chloride of ethyl are essentially different bodies; and not less distinct are dibromide of ethylene and monobrominated bromide of ethyl, which I have obtained in the course of these experiments by the action of bromine on bromide of ethyl. But, on the other hand, the allied members of these two pairs of bodies are so closely related to each other, that, under the influence of powerful reagents, they not unfrequently yield exactly the same products of transformation. I may here refer especially to an interesting experiment of Beilstein, who has shown that dichloride of ethylene and monochlorinated chloride of ethyl, when treated with alcoholic potassa, undergo the same decomposition: both these compounds give up hydrochloric acid, being converted into chloride of vinyl.

The denomination, *bromethyl-triethylphosphonium,* which I have adopted for the metal produced by the action of dibromide of ethylene on triethylphosphine, involves to a certain extent the assumption that this body might, under favourable circumstances, be produced also by the mutual action of triethylphosphine and monobrominated bromide of ethyl. In a subsequent chapter of this inquiry I shall have an opportunity of showing how far this assumption is established by experiment.

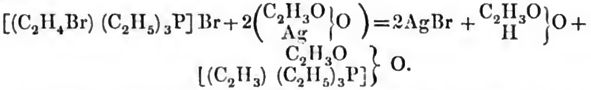
SALTS OF VINYL-TRIETHYLPHOSPHONIUM.

In tracing the history of the salts of bromethyl-triethylphosphonium, I have mentioned that these substances lose their latent bromine, though slowly, when boiled with silver-salts. I was curious to ascertain whether this reaction involves the same metamorphosis that the bromethylated body undergoes under the influence of oxide of silver.

In the anhydrous condition, the bromethylated bromide acts but slowly on acetate of silver. In the presence of alcohol or water, the reaction is rapidly accomplished at 100° C. The liquid filtered from the bromide of silver yields no further precipitate on addition of ammonia, showing that the whole of the bromine is eliminated. When evaporated with hydrochloric acid, the liquid abundantly evolves acetic acid. After sufficient concentration, it yields with dichloride of platinum a fine octahedral salt, which may be purified by crystallization. This salt contains:

$$C_8H_{18}PPtCl_3 = [(C_2H_3)(C_2H_5)_3P]Cl, PtCl_2,$$

It is thus seen that the action of silver-salts—at all events of acetate of silver—upon the bromethylated bromide differs from that of oxide of silver. While the latter gives rise to the formation of an oxethylated phosphonium, the former produces a phosphoretted metal in which three atoms of ethyl are associated with one atom of the radical C_2H_3, which may be termed vinyl. The product, then, which is formed by the action of acetate of silver upon the bromethylated bromide is the acetate of vinyl-triethylphosphonium:



$$[(C_2H_4Br)\ (C_2H_5)_3P]\,Br + 2\left(\left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\}O\right) = 2AgBr + \left.\begin{matrix}C_2H_3O\\ H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ [(C_2H_3)\ (C_2H_5)_3P]\end{matrix}\right\}O.$$

I have been satisfied to establish the formation and composition of the vinyl-compound by a careful and frequently repeated analysis of the platinum-salt, which had been obtained from the products of four different operations. The salts of vinyl-triethylphosphonium resemble the oxethylated compounds. I have prepared the iodide, which crystallizes, but is extremely soluble, even in absolute alcohol.

The formation of the vinyl-compound was observed in several other processes, which may here be briefly mentioned, although I must state at once that the experimental evidence on which these observations are based is less conclusive.

The oxethylated compound differing from the vinyl-triethylphosphonium-salt simply by the elements of one molecule of water, which the latter contains less, the question naturally suggested itself whether, under the influence of heat, the oxethylated compound might not be converted into the vinyl-body. The results of two experiments appear to answer this question in the affirmative. In one case, the bromide of bromethyl-triethylphosphonium had been boiled for a considerable time with oxide of silver. In another experiment, a concentrated solution of the oxethylated base was evaporated over an open flame until a very appreciable quantity was entirely decomposed. In both cases, it was proved by analysis that the oxethylated base had been transformed into the vinylated compound. In a third experiment, however, in which the temperature was not allowed to rise above 150°, the oxethylated compound was not altered.

The vinyl-compound appears to be formed also by the action of heat upon the bromethylated bromide:

$$[(C_2H_4Br)\ (C_2H_5)_3P]\ Br = [(C_2H_3)(C_2H_5)_3P]\ Br + HBr.$$

Torrents of hydrobromic acid are evolved, and the residue yields, after treatment with chloride of silver, on addition of dichloride, an octohedral platinum-salt. The decomposition is, however, completed only with difficulty. The evolution of hydrobromic acid continues for hours, even when the salt is kept at a temperature (between 235° and 250°), at which considerable quantities are entirely decomposed. I have thus been prevented from procuring an amount of the salt sufficient for its identification with the vinyl-compound obtained by the action of acetate of silver.

Vinyl-triethylphosphonium-salts are formed in one or two other reactions, which will be noticed in subsequent paragraphs of this inquiry.

SERIES OF DIATOMIC COMPOUNDS. DIPHOSPHONIUM COMPOUNDS.

Salts of Ethylene-hexethyl-diphosphonium.

Dibromide.—The occurrence of this salt among the products of the action of dibromide of ethylene on triethylphosphine has already been mentioned in the introduction to the experimental part of the memoir. On bringing together the materials in the proportions indicated by the equation

$$C_2H_4Br_2 + 2C_6H_{15}P = C_{14}H_{34}P_2Br_2,$$

that is to say, one volume of dibromide of ethylene and three volumes of the phosphorus-base, the diatomic compound is obtained, nearly in the theoretical quantity. It is distinguished from the monatomic product of the same reaction by its much greater solubility even in absolute alcohol, from which it separates only after almost complete evaporation, in needles which are permanent in the air. In ether this salt is insoluble, as are in fact most of the bromides of the phosphorus-bases, both monatomic and diatomic. The dibromide obtained by the direct action of dibromide of ethylene on triethylphosphine, always contains a small quantity of the monatomic bromide, from which it can only be purified with great difficulty. And further, if the dibromide of ethylene has not been carefully purified from adhering hydrobromic acid, the resulting salt is likewise contaminated with traces of the extremely soluble hydrobromate of the phosphorus-base, the presence of which likewise interferes very much with the purification of the product. Lastly, the formation of oxide of triethylphosphine can never be entirely avoided, even when the operation is conducted in an atmosphere of carbonic acid. To obviate these inconveniences, the compound submitted to analysis was prepared by saturating the hydrate, to be presently described, with hydrobromic acid.

The simplest expression of the results obtained in the analysis of this compound is the formula

$$C_7H_{17}PBr;$$

its formation, however, and its, deportment, fully to be discussed in the following paragraphs, prove unmistakeably that this expression must be doubled, and that the weight and composition of the molecule of this body is represented by the formula

$$C_{14}H_{34}P_2Br_2.$$

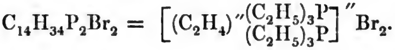
On comparing the composition of the two bromides which are formed from dibromide of ethylene by the fixation of one or two molecules of triethylphosphine, it could scarcely be doubted that the monatomic compound, even when already formed, must still be in a condition to take up the second molecule of triethylphosphine, and thus to pass into the diatomic bromide. The correctness of this supposition is easily established by experiment. The monatomic bromide acts strongly, even at ordinary temperatures, on a fresh quantity of the phosphorus-base, being transformed, with evolution of heat, into the diatomic compound,

$$C_8H_{19}PBr_2 + C_6H_{15}P = C_{14}H_{34}P_2Br_2.$$

In presence of alcohol and at 100°, the reaction is completed in a few seconds. With lively interest have I followed up the result of this simple experiment: for its success obviously pointed to a source from which an almost incalculable number of diatomic compounds of the most varied composition might be obtained.

For this reason I have not omitted to establish by numbers the conversion of the monatomic into the diatomic bromide, and in the following sections I shall have frequent occasion to quote results, which leave no doubt as to the facility of this transformation.

The molecular constitution of the new bromide is satisfactorily represented by the formula



$$C_{14}H_{34}P_2Br_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

The salt is derived from a diatomic metal, a diphosphonium, in which 6 equivs. of hydrogen are replaced by 6 equivs. of ethyl, and the remaining 2 equivs. of hydrogen by the radical ethylene indivisible under the given circumstances. It is the diatomic character of the ethylene that links together the two molecules of triethylphosphine, and gives to the new molecular system the necessary stability.

The dibromide is very easily attacked by silver-compounds, and in this manner an extensive series of very sharply characterized diphosphonium-salts may be obtained, many of which crystallize remarkably well. In these reactions, however, a tendency towards the formation of double compounds is frequently observed, and hence it is for the most part better to prepare the salts by treating the free base with the corresponding acids.

In examining the dibromide, I have made some observations which I may take an opportunity of pursuing further by and by. When the aqueous solution of this salt is mixed with bromine-water, very beautiful yellow needles are immediately separated, consisting of a polybromide. These needles may be recrystallized from boiling water, but apparently not without decomposition. They have but an ephemeral stability. On boiling the compound, bromine continues to be evolved, and ultimately the original bromide is left behind. Polybromides of exactly similar character are formed by the action of bromine on the bromides of all the ammonium- and phosphonium-bases that I have examined.

I have already pointed out that, in fixing one molecule of triethylphosphine to form the compound

$$[(C_2H_4Br)(C_2H_5)_3P]Br,$$

dibromide of ethylene exhibits a deportment which might have been expected from bromide of bromethyl, with which it is isomeric. It was of some interest to examine experimentally, the behaviour of triethylphosphine with monobrominated bromide of ethyl. This substance had never been prepared. I have obtained it, together with the dibrominated bromide of ethyl $(C_2H_3Br_2)Br$, by submitting bromide of ethyl to the action of dry bromine under pressure at a temperature of 180° C. Brominated bromide of ethyl is a heavy aromatic oil, boiling at 110° C., and consequently differing altogether from dibromide of ethylene, which boils at 130° C., and with which it is isomeric. The brominated bromide attacks the phosphorus-base much more slowly than the dibromide; the final result, however, is exactly the same, the bromide of the bromethylated monophosphonium and the dibromide of the ethylene-diphosphonium being produced. The former of these salts is obtained in comparatively small quantity, and I was therefore unable to identify the compound in question with the bromethylated bromide obtained by means of the ethylene-compound, otherwise than by the characteristic reaction with silver-salts, mentioned in an earlier paragraph of this paper. The diphosphonium-compound, on the other hand, is easily produced in sufficiently large quantity, by means of brominated bromide of ethyl. I had no difficulty in establishing the absolute identity of this compound with the product obtained from dibromide of ethylene, by a careful comparison of the chemical and physical properties of the substances, and moreover by the analysis of a di-iodide and a platinum-salt derived from the bromide-of-ethyl-derivative.

Dihydrate.—The free base is easily obtained by the action of oxide of silver on the dibromide, or better on the di-iodide, which latter is, of all the diphosphonium-compounds of this class, the easiest to obtain in the pure state. If the alcoholic solution of the crude dibromide be used in this experiment, the first portions of oxide of silver added to the liquid are completely dissolved, and the solution, which has already become alkaline, deposits a white crystallized double compound of the dibromide with bromide of silver, which, however, is completely decomposed by further addition of oxide of silver and dilution with water. In this manner, there is produced an extremely caustic, nearly odourless liquid, having a strongly alkaline taste, and exhibiting the bitterness which is so often observed in the analogous bodies of the nitrogen-series. In other respects, the base exhibits the properties which characterize the hydrates of tetrethylphosphonium* and tetrethylammonium.† The solution, when evaporated in an open vessel, rapidly absorbs carbonic acid, and ultimately yields a semi-crystalline mixture of dihydrate and carbonate. When evaporated *in vacuo* over sulphuric acid, the caustic solution gradually dries up to a syrupy, extremely deliquescent mass, which exhibits no traces of crystallization. On mixing the highly concentrated solution of the dihydrate with solution of potassa, the base is separated from the liquid in oily drops, which are, however, readily dissolved on addition of water. The free base, like the corresponding monophosphonium- and even monammoniumcompounds, cannot therefore be obtained in a state fit for analysis; its formation, however, as well as its conversion into a series of well-defined salts corresponding to the dibromide, characterize it as an oxide derived from the type,—

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* Phil. Trans. 1857, Part II. p. 583. Chem. Soc. Qu. J. xi. 65.

† Phil. Trans. 1851, Part. II. p. 357. Chem. Soc. Qu. J. iv. 304.

$$\left.\begin{array}{l} H_2 \\ H_2 \end{array}\right\} O_2,$$

as the hydrated dioxide of ethylene-hexethyl-diphosphonium:

$$C_{14}H_{36}P_2O_2 = \left.\begin{array}{c} [(C_2H_4)''(C_2H_5)_6P_2]' \\ H_2 \end{array}\right\} O_2.$$

Complicated as the construction of this compound must appear, it is remarkable for its stability. The solution may be boiled and considerably concentrated upon the water-bath without decomposition, and remains unchanged even when exposed for some time under pressure to a temperature of 150°; indeed the decomposition of the hydrate does not begin till the liquid is evaporated to dryness. The changes which this compound suffers under the influence of higher temperatures are not without interest. They are rather intricate, and I propose therefore to devote a special paragraph to their study.

In its deportment with metallic salts, the hydrate of the diphosphonium closely resembles the fixed alkalies, as may be seen from the following Table:—

Deportment of the Hydrate of Diphosphonium with reagents.

Barium-salts Strontium-salts Calcium-salts Magnesium-salts	White precipitates of the hydrates.
Aluminium-salts	White precipitate of hydrate of aluminium, soluble in excess of the precipitant.
Chromium-salts	Green precipitate of hydrate of chromium, soluble in an excess of the precipitant, and reprecipitated on ebullition.
Nickel-salts	Apple-green precipitate of the hydrate.
Cobalt-Salts	Blue precipitate of the hydrate.
Iron-salts —	
Ferrosum	Greenish precipitate of the hydrate.
Ferricum	Reddish-brown precipitate of the hydrate.
Zinc-salts	White gelatinous precipitate of the hydrate, insoluble in excess.
Lead salts	White amorphous precipitate of hydrate of lead, soluble in excess.
Silver-salts	Black-brown precipitate of oxide of silver.
Mercury-salts:—	
Mercurosum	Black precipitate of the suboxide.
Mercuricum	Yellow precipitate of the oxide.
Copper-salts	Light blue precipitate of the hydrate, insoluble in excess: in presence of sugar, the precipitate dissolves in excess, forming an azure-blue solution, from which, if glucose has been employed a red precipitate of suboxide of copper separates on ebullition.
Cadmium-salts Bismuth salts	White precipitates of the hydrates.

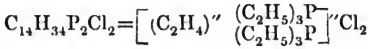
Tin-salts:	
Stannosum:—	
Chloride, containing free hydrochloric acid	White acicular precipitate of a double compound.
Stannicum:—	
Chloride . .	White gelatinous precipitate, extremely soluble in excess.
Antimony:—	
Trichloride . .	White acicular precipitate of a double compound.
Gold —	
Trichloride. .	Golden-yellow crystalline precipitate of a double compound.
Platinum:—	
Dichloride . .	Pale-yellow, slightly crystalline precipitate of a double compound.

These are, with few exceptions, the reactions of a solution of potassa. It is scarcely necessary to add that the hydrate of the diphosphonium expels, even at the common temperature, ammonia, phenylamine, triethylphosphine, and a considerable number of other amines and phosphines from their saline combinations.

The free base exhibits the deportment of caustic potassa towards iodine and sulphur. It dissolves crystals of *iodine* with facility; the colourless solution is neutral, and yields on evaporation a syrup-like half-crystalline mass, easily recognized as a mixture of the di-iodide with the di-iodate. Treatment with alcohol separates the crystals of the more difficultly soluble iodide from the gummy iodate. On adding concentrated hydrochloric acid to the liquid obtained by dissolving iodine in the free base, a dark-coloured substance (iodine or a periodide) is separated; after a few seconds, however, the liquid is decolorized and solidifies to a mass of beautiful lemon-yellow crystals. The diphosphonium-salts are thus seen to exhibit phenomena exactly similar to those which were observed by Weltzien in the case of the compounds of tetramethyl- and tetrethyl-ammonium. I hope to find an opportunity of returning to a more minute examination of the yellow compound, which, by recrystallization from boiling alcohol, may be obtained in splendid needles, and which will probably be found to be a compound of the di-iodide with chloride of iodine. For the present I may remark that similar compounds are formed by all the bases of the type ammonium and diammonium which I have examined, provided they belong to that class in which the substitution is complete. A variety of monophosphonium- and monarsonium-salts, and lastly of compounds of phosphammoniums and phospharsoniums, submitted to the same process, have furnished perfectly similar results. Hydrochloric acid occasionally produces crystalline precipitates in the concentrated solutions of the iodates, even of bases of incomplete substitution; these precipitates disappear, however, on addition of water, or on gently warming, and are essentially different from the compounds previously mentioned. *Sulphur* dissolves in a concentrated solution of the dihydrate, although with difficulty, to a yellow liquid, which precipitates the black sulphide from lead-solutions, and is decomposed by acids, with separation of sulphur and evolution of sulphuretted hydrogen. *Phosphorus* is not attacked by the solution of the dioxide, not a trace of phosphoretted hydrogen being evolved, even by protracted ebullition.

Disulphhydrate.—The solution of the base saturated with hydrosulphuric acid, when allowed to remain for some time over sulphuric acid *in vacuo*, dries up to a gummy mass, which exhibits as little inclination to crystallize as the dihydrate itself. When evaporated on the water-bath in contact with the air, the disulphhydrate is decomposed, the sulphur being oxidized; ultimately an imperfect crystallization of the sulphate remains behind.

Dichloride.—This salt is easily obtained by treating the dibromide or the di-iodide with chloride of silver, and also by saturating the free base with hydrochloric acid; it is extremely soluble in water and in alcohol, insoluble in ether. The concentrated solution solidifies over sulphuric acid into a mass of large and highly deliquescent crystalline plates of a pearly lustre, which may be exposed to a very high temperature (290° to 300°) without the slightest alteration. The salt is precipitated unchanged from its aqueous solution by potassa; it contains—



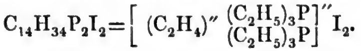
$$C_{14}H_{34}P_2Cl_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2.$$

The dichloride forms with metallic chlorides numerous well crystallized double compounds, some of which will be more particularly described hereafter.

The dichloride of the ethylene-diphosphonium is likewise produced by the action of monochlorinated chloride of ethyl, prepared, in accordance with Regnault's indications, by the action of chlorine upon chloride of ethyl. The chlorinated compound acts but slowly upon triethylphosphine at 100°. By digesting for twenty-four hours at 120°, a considerable proportion solidified to a white fibrous crystalline mass, which proved to be exclusively the dichloride of the diphosphonium. It was identified by conversion into the characteristic platinum-salt, and subsequently into the iodide, both of which were analysed.

Di-iodide.—This salt is perhaps the most characteristic of the diphosphonium-compounds. Crystallizing with peculiar readiness,—being easily soluble in hot, but sparingly soluble in cold water,—slightly soluble also in alcohol, and insoluble in ether,—it possesses all the properties which can facilitate the preparation of a pure and definite substance. It has therefore, for the most part, served as a starting-point in the preparation of the diphosphonium-compounds.

I have already remarked that, in the preparation of the monatomic bromide, the formation of the dibromide can scarcely ever be entirely prevented. The mother-liquors, remaining after numerous preparations of the monatomic bromide, were therefore united and treated with oxide of silver, whereby a caustic liquid was obtained, containing the hydrate of the diphosphonium, contaminated with the hydrate of the oxethylated monophosphonium arising from the decomposition of the bromethylated compound. These hydrates were converted, by saturation with hydriodic acid, into the corresponding iodides, the separation of which presented no further difficulty, inasmuch as the iodide of the oxethylated monophosphonium is extremely soluble in water and in alcohol. The sparingly soluble di-iodide was easily obtained in a state of perfect purity by several crystallizations. The crystals are anhydrous. Any hygroscopic moisture that may adhere to them is most conveniently removed by drying them over sulphuric acid, since the salt begins to turn slightly brown at 100°. Analysis proves this iodide to be represented by the formula,—



$$C_{14}H_{34}P_2I_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix} \right]'' I_2.$$

The di-iodide crystallizes from boiling water in needle-shaped crystals, which often attain a considerable size. Quintino Sella has communicated to me the following results, which he has obtained on examining these crystals :—

" System trimetric :—

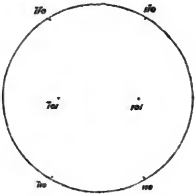
001, 101 = 45° 9′

100, 110 = 60° 18′

Forms observed :—

110, 101 (Fig. 41).

Fig. 41.



M M = 119° 40′; *b* : *h* = 1 : 0·8732.

Forms observed :—

M *é*..

Combinations observed :—

110, 101 (Figs. 42, 43). 110, 101 with other faces, too much rounded for their correct determination (Fig. 44).

Fig. 42.

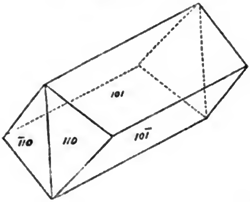


Fig. 43.

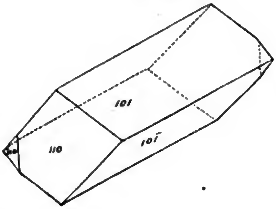
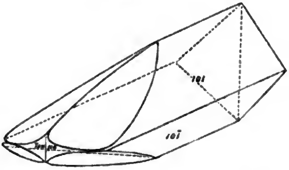


Fig. 44.



Cleavages 1 1 0 und 1 0 1 distinct, and easily obtained.

The crystals are long needles; the faces 1 1 0 are often but little developed (Fig. 43); they have then a monoclinic aspect; but the measurement of the angles 1 1 0, 1 0 1, and $\bar{1}$ 1 0, $\bar{1}$ 0 1, has furnished nearly the same result; and moreover, on examining the crystals with the polarizing microscope, the line [0 1 0] is found to be nearly one of the axis of elasticity.

The angle 1 0 1, $\bar{1}$ 0 1 is so near to 90°, that there might appear some reason for regarding the crystals as dimetric hemihedrals. I am not, however, of this opinion, for I have observed, only two cleavages, 1 1 0, $\bar{1}$ 1 0, instead of the four corresponding to the dimetric system; moreover the angle 1 0 1, $\bar{1}$ 0 1 has *always* been found a little greater than 90°.

The needles, when small, are transparent; the larger ones are rather milky, and hollow inside.

The lustre of the faces 1 0 1 is slightly nacreous, that of the faces 1 1 0 is vitreous."

The di-iodide, as already observed, is very much more soluble in boiling water than in cold water. 100 parts of boiling water dissolve 458·3 parts of the salt, of which only 3·08 parts remain in solution at 12°. A remarkable character of the salt is its insolubilitity in moderately concentrated solution of potassa; the dilute solution mixed with potassa immediately yields a crystalline precipitate; the same property is exhibited, as is well known, by the iodides of tetrethylammonium and of the other ammonium- and phosphonium-metals. The solution of the di-iodide, like those of the diphosphonium-salts in general, is perfectly neutral; it is colourless when first prepared, but on exposure to light soon acquires a tint of yellow, and finally turns brown, at the same time depositing a reddish compound, doubtless analogous to the periodides, which, as I observed some time ago, are formed under similar circumstances from the iodides of tetramethyl- and tetrethyl-ammonium, and which have since been so successfully studied by Weltzien. This red compound is immediately precipitated on adding a solution of iodine to the colourless solution. The di-iodide, like most diphosphonium-compounds, exhibits great stability. It melts, without the slightest decomposition, at 231°, and solidifies, with crystalline structure, a few degrees lower. When more strongly heated over an open flame it is decomposed, with formation of a red-brown substance, which I have not examined. On distilling the di-iodide with excess of caustic baryta in an atmosphere of hydrogen, triethylphosphine passes over: no gaseous product is formed in this reaction. Together with iodide of barium, which remains behind, and triethylphosphine which distils over, probably oxide of ethylene is formed in this reaction.

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2 + Ba_2O = 2\,Ba\,I + 2[(C_2H_5)_3P] + (C_2H_4)''O.$$

I should, however, state that I have not succeeded experimentally in tracing the formation of the oxide of ethylene.

An attempt to decompose the solution of the di-iodide with sodium-amalgam was unsuccessful; the salt, which is likewise but sparingly soluble in solution of soda, immediately separated out, and no appearances were observed which might have indicated the formation of the ammonium-amalgam. It is worthy of remark that no substituted ammonium-amalgam has yet been produced.

The di-iodide forms, with various metallic salts, crystalline double compounds, among which I have more particularly examined the zinc-salt; its analysis will be given further on.

Difluoride.—The solution of the hydrate, neutralized with hydrofluoric acid and dried over sulphuric acid, leaves a colourless transparent syrup, which does not crystallize, even after standing for a considerable length of time in air or *in vacuo*. The fluorine-compound, like the other diphosphonium-salts, is soluble in alcohol, but insoluble in ether.

Silico-fluoride.—The solution, neutralized with hydrofluosilicic acid, likewise failed to yield crystals by evaporation.

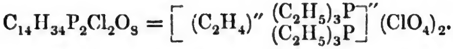
Dicyanide.—The solution of the hydrate, mixed with excess of hydrocyanic acid, retains its alkaline reaction; when evaporated on the water-bath, it gives off every trace of hydrocyanic acid. On digesting a solution of the di-iodide with excess of cyanide of silver, a double compound dissolves, which crystallizes in splendid needles, but is likewise decomposed by evaporation, with evolution of hydrocyanic acid and separation of cyanide of silver.

Disulphocyanate.—When a solution of the di-iodide is boiled with excess of recently precipitated sulphocyanate of silver, a solution of the disulphocyanate is obtained, perfectly free from silver, and solidifying by evaporation on the water-bath into a crystalline mass. The salt dissolves readily in water and in alcohol, and is precipitated therefrom by ether. The aqueous solution is likewise precipitated by potassa, the oily drops thus separated gradually solidifying into crystalline rosettes.

Dinitrate.—This salt, prepared by saturating the base with nitric acid, forms laminar crystals, permanent in the air, extremely soluble in water, less soluble in alcohol, and precipitated from the alcoholic solution by ether, as an oil which gradually solidifies. The solution forms with mercuric chloride, a precipitate which crystallizes in needles.

Diperchlorate.—This salt is perhaps the most beautiful of the diphosphonium-compounds. On mixing moderately concentrated solutions of the hydrate and perchloric acid, the liquid is soon traversed by delicate crystalline needles, often an inch long. They may be recrystallized from boiling water and dried at 100° without decomposition. At a higher temperature, they are decomposed, with slight detonation.

The analysis of the perchlorate, in which the diphosphonium was weighed in the form of the nearly insoluble platinum-salt, led to the formula:—



$$C_{14}H_{34}P_2Cl_2O_8 = \left[(C_2H_4)'' \begin{matrix} (C_2H_5)_3P \\ (C_2H_5)_3P \end{matrix} \right]'' (ClO_4)_2.$$

Di-iodate.—The base, neutralized with iodic acid and evaporated over sulphuric acid, yields an extremely deliquescent syrup which crystallizes but gradually. Solution of potassa separates the hydrate from the concentrated solution, in oily drops, sparingly soluble crystalline iodate of potassium being at the same time precipitated. The solution, mixed with hydrochloric acid, yields the lemon-yellow crystalline compound already mentioned.

Carbonate.—The solution of the oxide remains alkaline, even after saturation with carbonic acid; on evaporation, it leaves a mass having a slightly crystalline structure.

Sulphate.—Radio-crystalline, extremely deliquescent salt. Repeated attempts to produce diphosphonium-alums by mixing the solution with the sulphates of aluminium and chromium were unsuccessful.

Chromate.—The solution of the base, neutralized with pure chromic acid, deposits, when exposed to an atmosphere dried by sulphuric acid, extremely soluble needles arranged in stellated groups. With excess of chromic acid, nothing but an uncrystallizable syrup is obtained.

Oxalate.—Both the acid and the neutral solution of the base in oxalic acid dries up to a slightly crystalline mass.

Phosphate.—The di-iodide, boiled with excess of phosphate of silver, yields a neutral solution of the phosphate of the diphosphonium, which remains as a slightly crystalline mass when the solution is evaporated. Crystallization is not promoted by addition either of free phosphoric acid or of the hydrate.

Tartrate.—Extremely soluble; difficult to crystallize.

Dipicrate.—The aqueous solution of picric acid, added to a moderately concentrated solution of the hydrate, instantly produces a yellow crystalline precipitate, which separates from the boiling alkaline solution in long needles.

The diphosphonium-salts form a long series of double compounds, most of which crystallize splendidly.

Platinum-salt.—The solution of the dichloride, even when extremely dilute, yields with dichloride of platinum a pale-yellow precipitate, which appears amorphous to ordinary observation, but when examined under a microscope of rather high power, resolves itself into small prisms. This salt is nearly insoluble in cold and even in boiling water, so that, as already observed, the diphosphonium may be quantitatively estimated in this form. The precipitate dissolves, though with difficulty, in concentrated hydrochloric acid, and crystallizes from the solution, by slow cooling, in small but well-defined crystals of a bright orange red colour.

Quintino Sella has examined these crystals, and obtained the following results:—

" System monoclinic:—

$$100,\ 001 = 82^\circ\, 36'$$

Forms observed:

100, 010, 001 (Fig. 45).

Fig. 45.

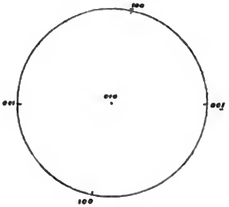
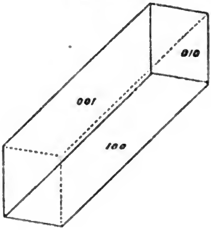


Fig. 46.



Combinations observed:—

100, 010, 001 (Fig 46).

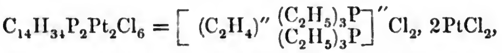
Cleavages 1 0 0, 0 1 0, 0 0 1 distinct and easily obtained, more especially 0 1 0.

The crystals are elongated in the direction of the axis of symmetry, and often hollowed out for a great part of their length when rather thick, that is to say, when their sides attain the width of half a millimetre. The hollow has the form of a pyramid having its base on the face 0 1 0 and its apex towards the centre of the crystal. The face 0 1 0 is often reduced to a very narrow rectangular rim. The opposite apex of the crystal is irregular, as if it had adhered to the side of the vessel. The face 0 0 1 is in general rather more developed than 1 0 0.

The crystals are optically negative. The plane of the optical axes is parallel to the line of symmetry [0 1 0]; the principal medium line is perpendicular to the latter and forms an angle of about 30° with a line normal on face 0 0 1. In fact, a plate parallel to 0 1 0 stops the passage of a ray of polarized light in that direction. Moreover, rings are observed through the faces 0 0 1 and in a plane parallel to the line of symmetry 0 1 0, and rather inclined towards a line normal on each face. The angle of the optical axis seen in this manner through the faces 0 0 1 appears to be very nearly 110°.

The crystals have a very fine orange-colour and a vitreous lustre."

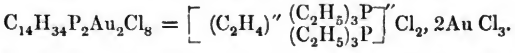
This platinum salt by numerous analyses was found to contain:—



$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix} \right]'' Cl_2,\ 2PtCl_2,$$

Palladium-salt.—A dilute solution of the dichloride is not precipitated by chloride of palladium. On concentrating the mixture and allowing it to cool slowly, reddish-yellow prisms make their appearance: by rapid evaporation a brick-red crystalline powder is obtained. Alcohol added to the aqueous solution of the two salts throws down the double salt as a chocolate-coloured crystalline magma composed of small interlaced needles. I have not analysed this compound.

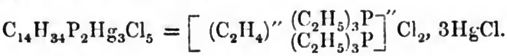
Gold-salt.—Beautiful golden-yellow needles, difficultly soluble in cold, easily soluble in boiling water and containing



$$C_{14}H_{34}P_2Au_2Cl_8 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix} \right]'' Cl_2,\ 2Au\ Cl_3.$$

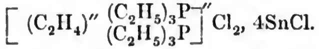
Mercury-salt.—Delicate crystalline needles or laminæ sparingly soluble in water and in alcohol, obtained by mixing the chloride of the diphosphonium with mercuric chloride.

Analysis led to the formula



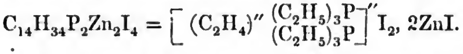
$$C_{14}H_{34}P_2Hg_3Cl_5 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix} \right]'' Cl_2,\ 3HgCl.$$

Tin-salt.—This salt, which is prepared like the mercury-compound, crystallizes from water in large well-formed prismatic crystals. According to some determinations, which, however gave only approximate results, the tin-salt appears to have the composition:



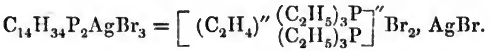
$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 4SnCl.$$

Di-iodide and Iodide of Zinc.—On mixing the two solutions, a crystalline precipitate is obtained, which separates in long needles when recrystallized from boiling water. The salt, which is apt to assume a yellowish coloration, contains



$$C_{14}H_{34}P_2Zn_2I_4 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2,\ 2ZnI.$$

Dibromide and Bromide of Silver.—I have mentioned this salt already when describing the preparation of the hydrate from the dibromide. When oxide of silver, which should not be mixed with too much water, is added in small portions to a boiling concentrated solution of the dibromide in alcohol as long as it dissolves, the filtered solution deposits on cooling white crystals, which contain



$$C_{14}H_{34}P_2AgBr_3 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2,\ AgBr.$$

The salt crystallizes, but not readily, from boiling alcohol. It is immediately decomposed by water, bromide of silver being separated, and the bromide of the diphosphonium passing into the solution.

In describing the general character of the action of dibromide of ethylene upon triethylphosphine, I have mentioned that, in addition to the monatomic and diatomic bromides, which are the principal products of the reaction, secondary compounds may be formed, but always in comparatively small quantities. The mother-liquors generally contain oxide of triethylphosphine, formed by the action of the atmosphere; they contain, moreover, bromide of triethylphosphonium, if the dibromide had not been carefully deprived of hydrobromic acid. The bromide of triethylphosphonium, however, under certain conditions, arises from the decomposition of dibromide of ethylene into hydrobromic acid and bromide of vinyl, the latter producing in this case the bromide of vinyl-triethylphosphonium. I had an opportunity of establishing this fact experimentally, when preparing a considerable quantity of the dibromide of the diphosphonium. The phosphorus-base having been employed in excess in this operation, not a trace of the bromethylated monophosphonium had been formed: its absence was carefully proved by a special experiment. The bromides were then transformed into chlorides and the latter precipitated by dichloride of platinum; the mother-liquor filtered off from the copious precipitate of the diphosphonium-salt was considerably evaporated, when, on cooling, well-formed octohedra were deposited, which on analysis were found to contain

$$[(C_2H_3)(C_2H_5)_3P]Cl,\ PtCl_2.$$

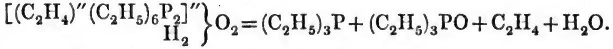
The formation of the vinyl-compound under these circumstances is easily explained:

$$C_2H_4Br_2 + 2[(C_2H_5)_3P] = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HP]Br.$$

The amount of vinyl-compound produced is but very small in proportion to that of the other salts which are formed in the mutual action between triethylphosphine and dibromide of ethylene.

ACTION OF HEAT UPON THE HYDRATE OF THE DIPHOSPHONIUM.

The hydrate, when submitted to the action of heat, undergoes a series of remarkable changes, which I have studied with lively interest. The decomposition commences at 160°; on raising the temperature gradually to 250°, the whole of the hydrate passes over in the form of liquid and gaseous products. The liquid product consists of triethylphosphine and oxide of triethylphosphine; the gas contains a considerable proportion of ethylene, which is readily characterized by its deportment with bromine. This transformation may be represented by the following equation:



$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3P + (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The study of the changes, however, through which the hydrate runs before it is broken up, shows unmistakeably that this equation can represent but one phase, even of the final transformation of the diphosphonium-compound. The study of the intermediate changes presents unusual difficulties, and I confess at once that I have failed to solve the problem to my entire satisfaction.

The experiments carried out with the view of disentangling the intricacies of these reactions, will perhaps be better understood if I commence by setting forth the ideas which I have ultimately formed of these metamorphoses, and then describe the experiments on which they are founded.

Under the influence of heat, the hydrate of the diphosphonium undergoes two principal transformations, which are accomplished side by side. A portion of this compound gives rise to the formation of oxide of triethylphosphine and hydrate of tetrethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\ H_2\end{matrix}\right\} O_2 = (C_2H_5)_3PO + \left.\begin{matrix}[(C_2H_5)_4P]\\ H\end{matrix}\right\} O,$$

the latter splitting ultimately into oxide of triethylphosphine and hydride of ethyl,

$$\left.\begin{matrix}[(C_2H_5)_4P]\\ H\end{matrix}\right\} O = (C_2H_5)_3PO + (C_2H_5)H;$$

while a second portion is resolved into triethylphosphine and hydrate of oxethyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''C_2H_5)_6P_2]''\\ H_2\end{matrix}\right\} O_2 = (C_2H_5)_3P + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\} O.$$

The latter may undergo, at a high temperature, a further transformation, separating, partially at least, into water and hydrate of vinyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\} O = \left.\begin{matrix}H\\ H\end{matrix}\right\} O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\ H\end{matrix}\right\} O,$$

the vinyl-compound yielding, in the last stage of the reaction, oxide of triethylphosphine and ethylene,

$$\left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\ H\end{matrix}\right\} O = (C_2H_5)_3PO + C_2H_4.$$

The separation of triethylphosphine and its oxide by the action of heat upon the hydrated diphosphonium requires no special experimental demonstration. To individualize the other compounds, the following experiments were made:—A considerable quantity of the dihydrate was evaporated in a retort in an atmosphere of hydrogen. As soon as the phosphorus-base began to distil freely—at about 190°—the operation was interrupted, and the residuary alkaline liquid saturated with hydrochloric acid and precipitated with dichloride of platinum. A dingy yellow amorphous precipitate was thrown down, insoluble in cold water; and the mother-liquor, on evaporation, furnished a mass of deep orange-red octohedra, which were transformed into the corresponding iodine-compound. The salt thus obtained proved unmistakeably a mixture of two compounds of different solubility. The less soluble was obtained in beautiful crystals, exhibiting all the characters of iodide of tetrethylphosphonium. The formation of a tetrethylphosphonium compound, in this reaction, was identified by the analysis of the iodide, the platinum-salt and the gold-salt.

The result of analysis was most satisfactorily confirmed by the crystallographical examination of the salts under consideration. Q. Sella has compared the crystals of the iodide above mentioned with crystals of iodide of tetrethylphosphonium obtained in the usual way. I have appended at the conclusion of this paper the elaborate investigation of this beautiful salt, with which my friend has furnished me.

Far less conclusive is the experimental evidence which I was enabled to collect in support of the opinion, that the hydrate of tetrethylphosphonium formed by the action of heat on the hydrated diphosphonium is accompanied by the oxethylated triethylphosphonium compound. The principal argument in favour of this view is the abundant evolution of triethylphosphine, which cannot be understood unless we assume the simultaneous formation of the oxethylated, or of the vinyl-compound. I have failed in my endeavours to prepare the more soluble iodide which accompanies the tetrethylphosphonium-compound in a state of purity. Nor was the attempt to separate the two compounds in the form of platinum-salts rewarded by better success. Both platinum-salts crystallize in octohedra which differ but slightly in solubility.

The experimental numbers obtained in the analysis of these octohedra characterize a mechanical mixture of the two platinum-salts.

The action of heat upon the hydrate of the diphosphonium induces yet another transformation, to which I have already alluded when mentioning the dingy yellow insoluble precipitate which is formed on addition of dichloride of platinum to the product of the action of heat upon the hydrate, neutralized with hydrochloric acid.

The following paragraph contains the fragmentary information which I have collected in studying these changes.

PARADIPHOSPHONIUM-COMPOUNDS.

The basic compound which yields the amorphous yellow platinum-salt repeatedly mentioned, is a transient product of the action of heat on the hydrated diphosphonium. If during distillation, the alkaline residue in the retort be tested from time to time with dichloride of platinum, a point is soon reached, when instead of the slightly crystalline precipitate, perfectly insoluble in dilute hydrochloric acid, which appears at the commencement of the operation, an amorphous, generally dingy yellow precipitate is obtained, immediately dissolving on addition of a few drops of dilute hydrochloric acid. If the distillation be now interrupted, and the residue neutralized with hydrochloric acid, and mixed with a few drops of dichloride of platinum, a discoloured precipitate is thrown down, the filtrate from which, on addition of a further quantity of platinum-solution, yields the amorphous salt, of a light yellow colour, and in a state, of purity. This salt exhibits no trace of crystalline structure, even when examined under the most powerful microscope: in the perfectly dry state, it is remarkably electrical, flying about in all directions during trituration.

The same substance is obtained when the hydrated oxethyltriethylphosphonium is submitted to the action of heat. By interrupting the process at a convenient time, and adding dichloride of platinum to the neutralized residue, phenomena identical with those just mentioned are observed.

The compound which produces the amorphous yellow precipitate was lastly obtained, under the following circumstances.

While I was engaged with the study of the vinyl-compounds, the examination of which is described in one of the previous paragraphs of this paper, the idea suggested itself that the bromide of vinyl-triethylphosphonium might also be formed by the action of bromide of vinyl (C_2H_3Br) on triethylphosphine:

$$(C_2H_5)_3P + C_2H_3Br = [(C_2H_3)(C_2H_5)_3P]Br.$$

In performing the experiment, I had an opportunity of observing the sluggishness of action of this bromide, often previously noticed in experimenting in the ammonium-series. When gaseous bromide of vinyl is passed through triethylphosphine, not a trace of it is fixed by the phosphorus-base. Triethylphosphine may be distilled in an atmosphere of the bromine-compound without undergoing any alteration. Bromide of vinyl, freed from every trace of adhering dibromide of ethylene by repeated distillation at a low temperature, and subsequent washing with lukewarm water, was therefore enclosed, together with triethylphosphine, in a strong glass tube. No change was perceptible after two days' digestion at 100°; and it was only on the third day that a thin layer of viscid matter began to separate at the bottom of the tube. The digestion was then continued at a higher temperature; and after the mixture had been exposed for three days longer to a temperature varying from 160° to 180°, about half the fluid was found to be converted into a solid mass, while a limpid liquid floated on the top. On opening the tube, cooling it well at the time, the liquid effervesced strongly, and a gas escaped which burned with a green-edged flame, and appeared to consist, partly at all events, of the vapour of unaltered bromide of vinyl. In subsequent repetitions of the experiment, it frequently happened that the tubes were shattered by the sudden expansion of the compressed gas: hence probably permanent gases are formed in the reaction. The liquid decanted from the solid proved to be a mixture of undecomposed bromide of vinyl with free phosphorus-base; the solid mass was found to consist of several bodies. On dissolving it in water, a rather small quantity of a sparingly soluble, beautifully crystalline, nacreous salt separated out, the composition of which is at present undetermined. By treatment of the filtered solution with oxide of silver, a strongly alkaline liquid was produced, which, when neutralized with hydrochloric acid and precipitated with dichloride of platinum, gave at once the amorphous yellow platinum-salt easily soluble in dilute hydrochloric acid.

On analysis, this salt furnished results which characterize the platinum-compound of ethylene-hexethyl-diphosphonium.

Nevertheless the two substances are not identical. In addition to the difference in the physical properties and in the behaviour with dilute hydrochloric acid, the two salts exhibit other well-defined marks of distinction. The crystalline salt is perfectly insoluble in water, even when boiling. The amorphous salt dissolves readily, and is deposited again on cooling in the same amorphous condition. In designating this peculiar molecular variety as paradiphosphonium-compound, I simply wish to distinguish it from the salt of the ordinary diphosphonium, without giving any opinion respecting the nature of the difference. The existence of the diphosphonium-compounds in the crystalline and in the amorphous condition, reminds us of the behaviour of some of the native organic bases under the influence of heat. It is well known that several of these substances, which are remarkable for their powers of crystallization, are rendered perfectly amorphous when heated for some time above their melting-point.

As might have been expected, the paradiphosphonium-compounds are slowly and gradually reconverted into the ordinary diphosphonium-salts.*

The hydrated paradiphosphonium, when separated from the platinum-compound by successive treatment with sulphuretted hydrogen and oxide of silver, yields with hydriodic acid a gummy mass which only gradually assumes the crystalline form. By a considerable number of recrystallizations, the characteristic di-iodide was ultimately obtained with all its properties; when converted, by treatment with chloride of silver, into the dichloride, and precipitated by dichloride of platinum, it immediately yielded the well known crystalline precipitate so frequently mentioned in this paper. Both salts, the iodide and the platinum salt, were identified by analysis.

The transition of a diphosphonium-compound from the crystalline to the amorphous, and from the amorphous to the crystalline condition, appears intelligible enough†. The transformation of the oxethylated monophosphonium, however, into a diphosphonium-compound, and the formation of the latter by the action of bromide of vinyl upon triethylphosphine, claims our attention for a moment.

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* In several experiments, the reaction between bromide of vinyl and triethylphosphine gave rise to the formation of a mixture of the amorphous and crystalline diphosphonium-compounds.

† The diphosphonium-salt, which is formed by the action of sulphocyanate of ethylene upon triethylphosphine (Chem. Soc. Qu. J., vol. xiii. p. 320,) in the first place, likewise yields the amorphous platinum-salt when precipitated by dichloride of platinum.

The conversion of the hydrate of oxethyl-triethylphosphonium* into the hydrated diphosphonium is readily understood, if we remember that two molecules of the former contain the elements of one molecule of the latter and of one molecule of ethylene-alcohol:

$$2\left(\left.\begin{matrix}[(C_2H_5O)\,(C_2H_5)_3P]\\ H\end{matrix}\right\}O\right) = \left.\begin{matrix}[(C_2H_4)''\,(C_2H_5)_6P_2]''\\ H_2\end{matrix}\right\}O_2 + C_2H_6O_2.$$

I am unable to say whether the group $C_2H_6O_2$ actually separates as ethylene-alcohol, or, which is more probable, in the form of water and oxide of ethylene, or even of aldehyde. Material and patience began to fail when I had reached this point, and I must reserve the decision of this question to later experiments†.

The same remark applies to the final elucidation of the reaction between triethylphosphine and bromide of vinyl, which, as I have pointed out, likewise gives rise to the formation of diphosphonium-compounds. Two molecules of triethylphosphine and two molecules of bromide of vinyl contain the elements of one molecule of dibromide of the ethylene-diphosphonium and one molecule of acetylene:

$$2[(C_2H_5)_3P] + 2C_2H_3Br = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\ (C_2H_5)_3P\end{matrix}\right]''Br_2 + C_2H_2;$$

and experiment proves that a considerable amount of permanent gas is generated in this reaction; but there are other products formed, and it would be idle to dwell any longer on the interpretation of these unfinished observations.

In conclusion, I append Q. Sella's crystallographical examination of the iodide of tetrethylphosphonium, to which I have

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* I need scarcely mention that the purity of the compound used in my experiments had been established by a special analysis. When prepared from imperfectly purified bromethylated bromide, the oxethylated base is apt to contain minute quantities of the hydrate of the diphosphonium.

† The convertibility of the oxethylated triethylphosphonium-salts into diatomic compounds has induced me to try whether the action of triethylphosphine upon them would accomplish this transformation;

$$\left.\begin{matrix}[(C_2H_5O)\,(C_2H_5)_3P]\\ H\end{matrix}\right\}O + (C_2H_5)_3P = \left.\begin{matrix}[(C_2H_4)''\,(C_2H_5)_6\,P_2]''\\ H_2\end{matrix}\right\}O_2.$$

But even when heated up to 150°, the two bodies remain unaltered; nor is there any action when the oxide is replaced by the bromide of oxethyl-triethylphosphonium.

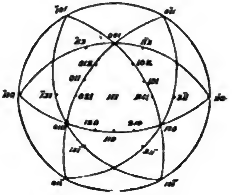
alluded in the latter portion of this paper, and also the results obtained by him in measuring the corresponding platinum-salt.

Crystalline form of Iodide of Tetrethylphosphonium.

"System rhombohedric :—
$1 1 1, 1 0 0 = 59° 32'$.

Forms observed :—
$1 1 1,\ 1 0 \bar{1},\ 1 0 0,\ 1 1 0,\ 2 1 0,\ 3 1 \bar{1}$
(Fig 47).

Fig. 47.



Forms observed :—
$a', d', \mathrm{P}, b', b^2, e_3$.

Fig. 48.

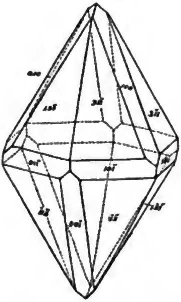


Fig. 49.

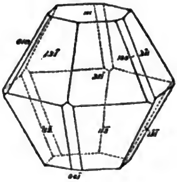
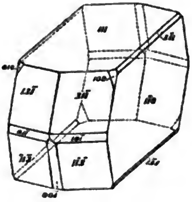


Fig. 50.



Combinations observed :—

$3 1 \bar{1};\ 1 0 0,\ 1 0 \bar{1}$ (Fig. 48).

$3 1 \bar{1},\ 1 1 1,\ 1 0 0$ (Fig. 49).

$3 1 \bar{1},\ 1 1 1,\ 1 0 \bar{1};\ 1 0 0$ (Fig. 50).

$3 1 \bar{1},\ 1 1 0,\ 1 0 0;\ 1 0 \bar{1},\ 2 1 0$ (Figs. 51 and 52).

$3 1 \bar{1},\ 1 0 0,\ 1 1 0;\ 1 0 \bar{1},\ 2 1 0,\ 1 1 1$.

The crystals prepared by treating triethylphosphine with iodide of ethyl exhibit the forms Figs. 51 and 52.

Fig. 51.

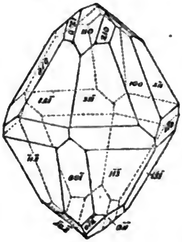
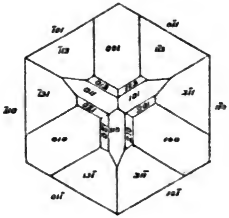


Fig. 52.



The crystals obtained by submitting the hydrated diphosphonium to the action of heat and neutralizing the alkaline residuary product with hydriodic acid, have the form Fig. 48, when rather large and slightly yellow, and the forms Figs. 49 and 50, when minute and perfectly white.

The crystals of the form Fig. 50 are most frequent; they seem to have adhered to the vessel with one of the larger faces of the prism $10\bar{1}$.

Crystals distinct. Lustre on the faces, except 1 1 1, very great.

Crystals optically positive. The indices of refraction are for the ordinary ray $\omega = 1{\cdot}660$, for the extraordinary ray $\epsilon = 1.668$.

The crystals of iodide of tetrethylphosphonium are isomorphous with those of iodide of silver. In the latter substance, 111, 100 = 58° 27′, instead of 59° 32′, found in the tetrethylphosphonium-salt. Both salts have the same hexagonal habitus, and both are optically positive."

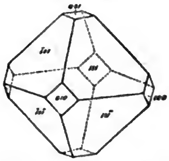
Crystalline form of the Platinum Salt of Tetrethylphosphonium.

"System monometric:—

Forms observed:—

100, 111 (Fig. 53).

Fig. 53.



The faces of the cube 1 0 0 are very brilliant; those of the octohedron 1 1 1 are often hollow.

No influence on polarized light.

Colour orange-red."

IX.—*On the Ice found under the surface of the Water in Rivers, called Ground Ice.*

By Richard Adie. Liverpool.

The ice found in the bed of a river or running stream under the surface of the water, is a subject which has engaged the attention of men of science, to endeavour to account for its occurrence in an apparently unnatural position, while it has also forced itself on the attention of practical men, on account of the mischief which an accidental obstruction, such as a branch of a tree lodged in the bed of a mill-course has been found to occasion when the water is charged with ice particles.

I believe that I was among the first to state that ground-ice is formed in the coldest part of a stream, and that the small crystals, immediately after they are formed, are carried along by the current, submerged and entangled by plants or other obstructions in the bed of the stream suitable for their detention.

In the recent frost of December and January 1860–61, I searched for ground-ice where, in past years, I had found it. Yet, though this frost was the most severe that has visited us during the sixty years of the century, I found ground-ice only in one locality,—a shaded place, where I was induced to search for it from seeing bundles of ice-crystals floating down the stream; for I had before observed that where ground-ice exists, some of it is constantly breaking off from the moorings. In this instance, the ice surrounded a stone covered over by the water of a rivulet which leaves the Marquis of Abercorn's grounds at Duddingston, near Edinburgh.

The other streams which I examined in the neighbourhood of Edinburgh shewed no floating crystals or other indications of the presence of ground-ice; they appeared to be well supplied with water, which, coming from underneath a covering of snow, was unfavourable for showing this kind of ice.

In the frosts of 1854 and of 1855, I found ground-ice in a number of rivers. These frosts differed from the recent one by penetrating into the ground to a greater extent. In 1854, the frost entered into the ground to the depth of 11½ inches, and that of 1855 to 13½ inches. In 1860-1 the earth had merely a crust of frozen soil under the snow.* The general calmness of the weather must likewise have had influence; for, in an exposed district in the neighbourhood of Liverpool, I have repeatedly found quantities of ground-ice after two days' moderate frost, accompanied by a dry brisk wind.

Those who have examined ground-ice appear to think that the water has frozen in the bed of the river, the current preventing it from freezing in its natural place—the surface. The appearance of the masses formed do not favour this view: for many shady positions in streams are noted for exhibiting collections of ice that could never have frozen there. To ascertain the nature of ice, when formed under water, on the sides of a containing vessel, I produced it rapidly by a freezing mixture, when the ice assumed a very hard form.

A small stream about twelve miles from Liverpool, where it joins the river Alt, is extremely favourable for showing the phenomena of ground-ice in an open exposed district. I first saw it there in December, 1846; and as I have since often examined the ice in the beds of streams, I wish to mention that the circumstance which appears to me most favourable for its formation, is wind accompanying the frost. On 13th December, 1846, the ground-ice was plentiful; my note at the time states that the frost had not been severe, but the air had been very dry, with a brisk wind.

Ground-ice is capricious both in its time and place of settlement. On 3rd January, 1854, I saw it in very large quantities in the bed of the Eden a little above Carlisle. In February, 1855, after a frost which had gone deeper down in the ground than the one of the previous year, I searched the same part of the Eden without seeing any; there were a sufficient number of loose ice crystals floating down the stream to render it probable that ground-ice existed higher up. On the same day I had seen ground-ice in the Ribble above Preston, but none in the Lune above Lancaster.

After I had become satisfied that the position of ground-ice is one of lodgment merely, I have been in the habit of searching for it where the streams pass under stone arches and places most unfavourable to freezing, and in these localities I have several times found it. The masses I have referred to, as seen in the Eden in 1854, must have been lodged there: for they contained throughout their substance a few water-worn pebbles, and they were all inclined towards the current from whence they were receiving continual supplies. I could not get at the collections of ice to measure them, as they were all under the surface in a deep-flowing part of the stream; but one rose so near the surface as to give a ripple to the current, and appeared to be from 4 to 6 feet high.

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* Since the above was written, the writer has been informed by a friend residing fifteen miles west of Edinburgh, where the snow was not so deep, that the frost in that locality penetrated the ground to the depth of an inch; and in a very few places, where the ground had been denuded of snow by the wind, the earth was frozen to the depth of thirteen inches.

Note on Mr. Adie's Paper "On Ground Ice."

By E. Frankland, F. R. S.

The formation of ground-ice has excited considerable interest amongst the observers of natural phenomena, and various suggestions have been made to account for its production. One of the most ingenious of these assumes that, in rapidly-flowing streams, the eddies and currents cause such a constant intermingling of the upper and lower water-strata, as to render the whole mass of the stream of one uniform temperature. When such a stream becomes cooled down to the freezing-point, the usual surface-layer of cold water below 39·5° F. cannot of course be formed. The rocks and other solid bodies in the bed of the stream continue, however, to radiate heat through the water into the atmosphere, and thus become reduced in temperature below the freezing point; the necessary consequence of such a state of things being the formation and gradual accumulation of ice around such solid bodies.

The latter part of this hypothesis appears to be untenable, inasmuch as water is absolutely intranscalent to rays of *obscure* heat: consequently, the passage of such rays from the bed of the stream through a stratum of water is absolutely impossible. It appears to me that the formation of ground-ice, which is well known to take place only in rapidly-flowing streams, depends upon the fact that ice, like other crystalline bodies, deposits itself more readily upon rough surfaces,—freezes, in fact, at a somewhat higher temperature when in contact with such surfaces, than within the mass of liquid itself. Hence, when a rippling stream is cooled to the freezing point, ice-crystals attach themselves to the pebbles and other objects in the bed of the river, these crystals forming equally inviting nuclei for the further deposition of larger quantities of ground-ice.

The tendency of ground-ice to form in shady places, as mentioned by Mr. Adie, is an interesting observation, which may probably find an explanation in the circumstance that water and ice, although perfectly unable to transmit obscure rays of heat, are yet to a certain extent transcalent to luminous heat. Tyndall has shown that certain interior portions of a block of ice may be melted by luminous heat, which has already passed through a considerable thickness of ice; and it is well known that if a mass of ice containing an embedded pebble be exposed to the solar rays, the ice around the pebble soon becomes melted. Any exposure, therefore, of ground-ice and its supernatant water to solar radiation would have the effect of warming the non-icy nuclei; thus remelting during the day, a portion, at least, of the ground-ice which had been formed during the previous night: consequently such an exposure must be regarded as presenting an obstacle to the formation of this kind of ice, although it is well known to favour the production of the ordinary surface ice.

X.—*On the Putrefaction of Bile, and the Analysis and Theory of Gallstones.*

By Dr. Thudichum.

In October, 1859, I communicated to the Medical Society of London a Paper, in which I described casts of the biliary ducts, which I had discovered in the centre of human gallstones. As these casts consisted principally of brown colouring matter of bile, or that modification of cholochrome termed *cholophaeine,* I first studied the chemical nature of that substance, in order the better to understand its bearing on the processes in which it played so conspicuous a part. The results of these inquiries I communicated to the Physiological Section of the British Association for the Advancement of Science, at the Oxford Meeting in 1860, and an abstract of my communication has appeared in the "British Medical Journal" for July 14th, 1860. I proved that cholochrome is an amido-acid; that it is decomposed by nitrous acid, with evolution of nitrogen, and yields a new acid—*cholochromic acid*,—which is free from nitrogen, and in its crystallized state resembles the substance termed by Virchow "hæmatoïdine," but, nevertheless, differs from it in many particular properties. I described several other products of decomposition and reactions of cholochrome, and, among them, the most important one, viz., that it is precipitated during the putrefaction of bile from the solution in which it was held by the healthy fluid. This led to the re-investigation of the process of putrefaction of bile, which had already been instituted by former observers; and I was not merely enabled to confirm the principal features of the description given by Gorup-Besanez, but also to add some new facts, explain the origin of some substances discovered by him, and construct a theory of this process of decomposition, which led me up, almost in a straight line, to the theory of gallstones. On subjecting large quantities of material to chemical analysis, these concretions yielded the same substances as those which made up the deposit of putrid bile, with the sole exception of mucus, of which little or none could be found in gallstones. Of these researches I gave a short account to the British Medical Association at their Annual Meeting, held in 1860, at Torquay. While able to accompany the leading ideas by the exhibition of specimens, progressively proving every step of my analyses, the limitation of the time imposed upon me by circumstances on that occasion did not permit me to do justice to the subject. I therefore more fully expounded my ideas before the Medical Society of London, in a Paper read before them on October 8th, 1860, and reported, in abstract, in the "British Medical Journal" for October 13th, and the contemporaneous numbers of the other medical periodicals. I then exhibited cholochrome, cholic acid, and earthy salts, as essential constituents of gallstones in man and animals. I characterized the cholesterine in gallstones of man as a secondary ingredient, calling for new analyses to prove the freedom from cholic acid of concretions reported to have consisted of pure cholesterine. Having come to the conviction that the binding material of gallstones is cholic and choloidic acid, I eliminated as untenable, the idea of an inspissation of mucus in the formation of these concretions, which had hitherto been the groundwork of all speculations upon their origin.

In the present communication I propose to give a short analysis of my results as a preliminary guide to the reader, and then to describe the chemical proceedings which I adopted for the purpose of ascertaining the composition of human and bovine gallstones and of ox-bile.

Theory of Gallstones.

In some examinations of human gallstones, I had found a resinous biliary matter; but, owing to the small quantity and the refractory nature of the substance, and particularly to the difficulty of separating it, I had not been able to identify it. The examination of some ox-gallstones afforded an opportunity for settling this point. I extracted a large quantity of cholic and choloidic acid from them,—a quantity such as could never be derived from any bile with which the calculi might be supposed to have been soaked at the time they were taken out of the gall-bladder. There could be no doubt that both cholic and choloidic acids had been deposited, together with the cholochrome, during the pathic process in the living animal.

The presence in almost all biliary concretions of some earthy and alkaline salts, points in the same direction. They are, and were, in my analyses, either present as phosphates and carbonates of lime and magnesia, and could be extracted by hydrochloric acid, or they were combined with the colouring matter of bile, and with stearic and palmitic acid. In gallstones from man, the colouring matter was accompanied by a larger proportion of inorganic salts; but in gallstones of the ox, the quantity of cholochrome preponderated to so extraordinary a degree over the earthy matter, that it must be assumed to be present in the free state, and not, as **Bramson** supposed it to be, always, viz., combined with lime.

Cholochrome, cholic, and choloidic acids, and earthy salts, thus present themselves as substances without the concurrence of which the more common forms of gallstones would rarely be formed; they are, in other words, essential ingredients of gallstones. In man, gallstones contain a large amount of cholesterine in most cases, but that is a secondary ingredient, as the phosphatic crust is of the uric acid, or oxalate of lime calculus from the urinary bladder, and is mostly crystallized around the other matters forming the nucleus. There are human gallstones, which, like those from the ox, contain no cholesterine. Others are said to consist entirely of cholesterine,—a statement which has to be verified by fresh analyses, which must prove the absence of cholic and choloidic acid. In gallstones from man, stearate and palmitate of lime are mostly present; and it remains to be seen how far those substances can assist in effecting the concretion of the detached particles of cholochrome, which I now ascribe to the cholic and choloidic acid. Let us therefore dismiss the hypothesis of the inspissated mucus, or the inspissated bile, which figure in our pathogeny as the mortar which combines the particles of the nucleus: mucus is not found in gallstones; and an inspissation in the midst of fluid bile is quite incomprehensible. Moreover, even an indubitable inspissation of bile could not lead to an insoluble concretion. We may, therefore, reject this hypothesis, and admit that *the binding material of the nucleus of gallstones is cholic acid, or choloidic acid, or both.*

The process by which gallstones are formed appears analogous to that which produces that rare description of calculus in the urinary passages,—the phosphatic or fusible calculus. It is a decomposition of the bile akin to putrefaction. The compound amido-acids split up into their constituents, under the influence of a cause which remains to be ascertained, but is probably a putrid ferment absorbed from the intestinal canal. Under the influence of a little acetic acid, formed out of glycocoll, and some other new acid produced by the putrefactive change, perhaps valerianic acid, cholochrome, a quantity of cholic acid, and a portion of choloidic acid, together with some salts and little fat, are deposited. This is the process in the ox, and sometimes in man. But the bile of man differs in this respect from that of the ox, that it contains cholesterine, while that of the ox contains, at the most, only a very small quantity as compared to the other. This cholesterine is dissolved in the taurocholate of soda. But as soon as the acid of this salt is decomposed, the cholesterine is set free, crystallizes, and deposits upon any particle that may happen to be within easy distance, in the manner of all crystals, which like to post themselves upon prominent bodies.

Numerous are the modifications which this process may undergo; but their discussion must be reserved for future occasions. The presence of chloride of sodium, iron, copper, and other inorganic matters in gallstones, has no doubt a significance in each case, but a subordinate one. In some gallstones from the ox, I have again found a sulphurous compound, already observed by Bolle in 1852. When boiled with hydrochloric acid, they gave out vapours which smelt like sulphuretted hydrogen, and blackened lead-paper. I collected them in caustic potassa, mixed with some solution of arsenious acid. On subsequent acidification, a yellow, somewhat orange-coloured deposit of a sulphur-compound of arsenic was formed; but after drying, it had become brown and hard, and on sublimation, yielded tersulphide of arsenic, besides leaving a quantity of charcoal; thus proving that the gas was a compound of a carbonaceous and a sulphurous body in a volatile form, or a mixture of two analogous substances.

Putrefaction of Bile.

Some large bottles, full of bile, and well stoppered, had been allowed to stand for the period of two years and one year respectively. The bile had assumed a feebly acid reaction, a bright port wine colour, and had deposited a copious flaky, green and brown deposit, mixed with white chalk-like particles and greenish crystals. This deposit, on analysis, was found to consist of cholochrome, cholic acid, phosphate of lime and magnesia in dichroic crystals, and mucus. The fluid part of the bile was found to contain principally choloidate of soda, with little cholate, taurine, valerianate, and acetate of soda and ammonia, phosphate of soda, but no glycocoll, nor any glycocholic or taurocholic acid. It was quite clear that the bile had spontaneously undergone a decomposition similar to that which is effected by boiling with acids or alkalies,—a decomposition which, in its main features, has already been described by Gorup-Besanez. Glychocolic and taurocholic acids had split respectively into glycocoll, taurine, and cholic acid. The cholate, probably, or some other decomposing substance, had yielded valerianic acid, which had combined with soda, or with ammonia, which latter probably originated in the decomposition of glycocoll. This compound being the amido-acid of acetic acid, no doubt in this process, as in the putrefaction of urine, yielded the acetic acid, which combined with the necessary amount of soda, and precipitated a portion of the cholic acid, while the greater portion of this acid remained in solution combined with soda, and became further metamorphosed into choloidic acid, and perhaps other products of decomposition of an acid nature. The cholochrome had no doubt been precipitated by the new acid before cholic acid, as its acid properties are much less pronounced.

The port wine colour of the fluid was probably due to some metamorphosed cholochrome, possibly cholochromic acid, or a derivate. That cholochrome, cholic acid, and crystallized phosphates are precipitated in this process had not been observed by Gorup-Besanez, who had also neither found valerianic acid, nor explained the origin of the acetic acid, which he undoubtedly discovered.* These observations, then, and the theory of the process, are my own additions to the doctrine.

Gorup-Besanez extracted also a mixture of fatty acids from putrid bile, among which he believed to have recognized margaric acid. This acid, or its fellow, stearic acid, is a component of the first deposit formed in putrid bile. But, like cholesterine in ox-bile, this ingredient is too easily lost sight of, in consequence of the small quantity in which it is present.

When Gorup-Besanez allowed bile to decompose at a temperature of from 25° to 30° R, exposed to the free access of the air, for a period of three weeks, he obtained choloidic acid as the principal product of decomposition. When, however, he exposed bile to the air for three months, in a cellar, at a temperature varying between 10° and 12° R, he found cholic acid instead of choloidic. In both cases, the decomposed mass had an offensive ammoniacal smell and a marked alkaline reaction. Taking into consideration only one element, viz., that of time, he concluded that choloidic acid was the forerunner of cholic acid; that the latter was produced from the former; that the presence of cholic acid was evidence of a more advanced stage of decomposition than that of choloidic acid. But he omitted to take into consideration the most important fact, —that the specimen of bile which yielded the cholic acid had been subjected to a much lower temperature than the specimens which yielded the choloidic acid, and had thus been influenced by circumstances which, above all others, retard the decomposition of animal matters. His assumption, therefore, while unsupported by any direct proof, is opposed by the fact, that we know choloidic acid only as a product of decomposition of cholic acid; that we cannot reproduce cholic from choloidic acid; and further, by the results of my own investigations, which showed that bile, after one year's, and after two years' decomposition, contained principally choloidic acid; a portion of this biliary element only being precipitated in the form of cholic acid. This precipitate, it is but right to conclude, was produced at a time when cholic acid prevailed: for had choloidic acid prevailed at the time of the formation of the new acid (acetic, valerianic, and others), the deposit must have consisted of choloidic acid, or at least contained some choloidic acid, while in fact it contained hardly any, or none. No cholic acid remained in solution. On account of these facts, I believe that we must reverse the order of succession assigned to those acids by Gorup-Besanez, giving to cholic acid priority in time, to choloidic acid ultimate supremacy, and ascribing to its break-up into the fatty acids above-mentioned the destruction of the biliary state.

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* Ann. Ch. Pharm. lix, 129.

Bile decomposed at a moderate temperature during nine months, was found by Gorup-Besanez to exhibit an acid reaction, due to the presence of acetic acid in a free state. It consequently had the same reaction as the specimens examined by myself. He does not state in what condition the biliary acid was present; which is much to be regretted, as free acetic acid could not be present so long as any cholate or choloidate remained in solution, the acids of which salts, in his analyses, he always precipitated by acetic acid.

Diagram exhibiting the Decomposition of Bile.

First Stage. The bile is neutral or alkaline.

Taurocholate of soda yields { Cholate of soda.
Taurine.

Glycocholate of soda yields { Cholate of soda.
Glycocoll.

Margarate (Palmitate) and stearate of lime
Phosphate of lime and magnesia } are deposited.

Second Stage. The bile becomes acid by the supervention of a new (valerianic?) acid, whose origin is undecided.

Cholate of soda deposits cholic acid.

Soda-salt of new acid is formed.

Cholochrome (Cholophaeic acid) is precipitated, and partly transformed into soluble cholochromate (?)

Glycocoll yields { Acetic acid.
Ammonia.

Third Stage. The bile continues acid.

Cholate of soda is transformed into choloidate. The latter deposits some choloidic acid (?).

Choloidate of soda yields fatty acids, products of decomposition; among them, probably derived from glycocoll, acetic acid, in the free (?) state.

The alkaline condition during the first stage, observed by Gorup-Besanez, occurs only when bile putrefies at a high temperature, so that the mucus undergoes active decomposition, and produces ammoniacal compounds. The bile upon which I operated, at low temperatures, and with moderate access of air, I could not at any time discover to be alkaline. In one case, Gorup-Besanez observed the acid reaction to give way to a second alkaline reaction, but did not notice any corresponding essential changes. Owing to these uncertainties, I have not distinguished as stages the neutral, alkaline, acid, and last alkaline conditions. Gorup-Besanez is of opinion that the decomposition of the primary biliary acids is not effected until an acid reaction of the bile appears; because only at that juncture does acetic acid produce a precipitate of cholic or choloidic acid. But this negative test appears to me only relative: because the acids may be decomposed, and yet acetic acid may produce no immediate precipitate, more acetic acid being required to cause a precipitate at the period when the bile is yet neutral or alkaline, and when no adventitious acid has yet taken the edge off the alkaline phosphate of soda, which is invariably present in bile, and though not very evident to test-paper, neutralises some acid before an acid reaction can become established. To the naked eye, the first stage is characterized by the deposition of white granules, partly on the top of the fluid, partly at the bottom, partly against the walls of the vessel, which consist of palmitate, stearate, and phosphate of lime. All the stages no doubt gradually pass into each other; and the above diagram, while considered useful for illustration, must not be considered as an absolute syllabus of a variable process.

Analysis of human gallstones.

I must here distinguish between the general analysis of gallstones, by which the essential constituents are found, and those special processes which are directed to the isolation of certain less frequent ingredients, such as copper, manganese, sulphides, or uric acid. Those human gallstones which consist principally of cholochrome, are to be analysed by the process which will be detailed lower down as applicable to gallstones from cattle. For the analysis of the common cholesterine concretion from man, the following process will be found suitable.

The powder of the calculi is gradually thrown into hot benzole, contained in a flask, placed on a sand-bath. The cholesterine and biliary matters are dissolved, while cholochrome, earthy phosphates, earthy salts of fatty acids, and any other ingredients remain suspended and unchanged. Solution and residue are separated by filtration. The matter on the filter is washed with repeated quantities of benzole, lastly with cold alcohol, and dried. It then presents itself as a brown powder, which is very delicate to the touch, imparting an almost velvety feel. Treated on the filter with absolute ether containing little nitric acid, it yields fatty acids to the ether, which, on distillation of the ether from the filtrate, are deposited in a granular and crystalline form. If the residue on the filter is next treated with water, phosphate and nitrate of lime and magnesia are extracted, and remain as phosphates and carbonates, sometimes coloured blue by copper, on evaporation of the solution and incineration of the residue. The colouring matter, extracted with ether and nitric acid and water, is free from fatty matter, but retains some earths, which can only be obtained by burning the cholochrome, or by dissolving it in carbonate of alkali, when the earthy and other insoluble inorganic and organic matters remain behind. They are then incinerated and the ashes added to the earths extracted by acid and water.

The carbonate of lime may be recognized by the effervescence, which takes place on dissolving the earthy salts in hydrochloric acid. The subsequent addition of ammonia in excess precipitates the phosphates, while the lime which before had been as carbonate, remains in solution, and may be precipitated by phosphate of soda or oxalate of ammonia. From the original benzole solution, cholesterine is best obtained by evaporating the solvent, and treating the residue with boiling spirit of wine. On cooling, the cholesterine, which before had been greenish, crystallises in the usual glistening white plates, while the solution retains the brownish-green coloured biliary matters. On evaporation, a small quantity of a mixture of cholesterine and fat is deposited. That and the rest of the alcohol being removed, there remains a brown resinous mass, insoluble in water, soluble in alcohol, and soluble in caustic potassa; an excess of caustic ley added to the solution causes the separation of a resinous salt, which floats on the top of the caustic fluid. From the solution in potassa, it is precipitated by hydrochloric acid. It combines with lime and baryta, forming insoluble compounds, and is therefore choloidic acid, though brown and impure, and perhaps, as suggested by the analysis of ox-gallstones, mixed with some cholic acid. It yields a small quantity of matter to boiling water; but the nature of this extract could not be determined by crystallization, as was the case in the analogous extract from ox-gallstones.

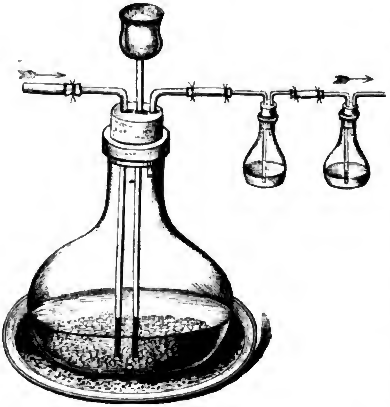
In his directions for analysing human gallstones, **Simon** refers hypothetically to the presence of biliary resin, without, however, stating its presence as a positive occurrence, or grasping its significance. In the ordinary analysis of gallstones, which began with the extraction of the powder by means of caustic potassa,—a process mainly directed to the purification of cholesterine, choloidic (and cholic) acid remained with the cholochloine produced, from which it could afterwards be scarcely separated. When the analysis of gallstones had, however, for its principal object the preparation of cholophaeine, the spirituous mother-liquor of cholesterine was not thought of sufficient importance to deserve further scrutiny; and even if it had been granted, it is possible that the fatty salts dissolved by the boiling spirit (which, in the analysis with benzole, remain undissolved, and are subsequently decomposed with acid and extracted with ether and water), would have made the separation of the choloidic acid a matter of considerable difficulty.

Analysis of ox-gallstones.

The gallstones are powdered, and boiled with water during three hours. The dark-brown extract is removed by filtration, and the residue on the filter washed during three days with boiling water, —that is, until the filtrate comes away colourless. The powder is then dried in the water-bath. The water-extract is evaporated.

It is then boiled for several hours with alcohol of 80° strength, which also acquires a dark colour, and is separated by filtration. The residue is for several days washed with boiling alcohol, and dried. The primary filtrate is allowed to cool by itself and the washings are evaporated by themselves. The alcoholic extract is further analysed, as will be detailed lower down.

The powder is next mixed with water in a flask, and a quantity of hydrochloric acid added. A slight frothing ensues, and the smell of sulphuretted hydrogen is at once perceptible; lead-paper is turned black by the gas. It is therefore necessary to perform the extraction with hydrochloric acid in a gas-evolution bottle, with funnel for the addition of the acid, and two tubes, one for passing a current of air through the acid fluid, the other for conducting the gases through an alkaline solution of arsenious acid, coloured blue by litmus. In my first analysis, this alkaline solution was contained in two bottles, and as soon as the acid vapours had coloured the litmus red, the first bottle was removed, the second bottle put in place of the first, and a new bottle in the place of the second. All the sulphuretted hydrogen was driven out of the mass by boiling, and a current of air was passed through the fluid, and absorbed in the alkaline fluid. The united solutions, on addition of an excess of hydrochloric acid, precipitated yellow flakes of a sulphur-compound of arsenic, which, collected on a filter, washed and dried, weighed 1·8 grains, corresponding to 0·743 grains of hydrosulphuric acid. On drying, this precipitate became brown and hard, and, on sublimation, yielded tersulphide of arsenic, as already stated, besides a quantity of charcoal. That so small a quantity of this sulphur-compound should have been obtained from about six ounces of gallstones is explained by the experience of Bolle, who analyzed two gallstones, only one of which yielded sulphuretted hydrogen.



The residue which remains after the removal of the hydrochloric acid extract, consists of cholochrome with traces only of the original admixtures.

The water-extract, on evaporation, yields a syrup, of a faintly acid reaction, mainly bile. It is soluble in water and spirits, and no crystalline organic compound is deposited from it, even after months of repose. But it has the remarkable property of holding in solution and at length depositing in well-defined, large crystals, phosphate of lime.

The alcoholic extract, on cooling, deposits a small quantity of white granular matter, which is collected on a filter, washed with alcohol, and dried. It consists of cholic acid, containing some fatty acid not easily separated. The filtrate has the property of ambergris, being amber in reflected, and green in transmitted light. It also has a most agreeable odour of musk. After a part of the alcohol has been distilled off, and the fluid has been again allowed to cool, flakes of crystalline matter are deposited. They probably consist of cholesterine. After further evaporation, a biliary acid is deposited in drops,—amorphous cholic acid. After prolonged standing, crystals of the same character as those obtained by alcohol from the deposit in rotten ox-bile are deposited,—crystallised cholic acid. Most of them are mixed with a syrup, from which they cannot be separated mechanically. This syrup is insoluble in water, and becomes resinous after contact with it: it has all the properties of choloidic acid. This mixture of acids is boiled for a long time with water, which dissolves cholic acid, and a light yellow matter,—perhaps choloidic acid, though this acid is reported to be quite insoluble in water. However that may be, the watery decoction, when left to spontaneous evaporation, which takes months, owing to the formation of a pellicle on the surface, at last deposits the very characteristic splendid needles of cholic acid, mixed with a granular brown deposit, which does not give the cholochrome reaction, and may be choloidic acid.

The hydrochloric acid extract is of a light brownish colour, and perfectly transparent. Evaporated on the water-bath, it deposits a black matter, which, after mixing with water, becomes brown, and consists of cholochrome, yielding the usual reaction. Several subsequent evaporations each yield some of this deposit, which ultimately becomes mixed with earths. The earths are phosphates of lime and magnesia, which are deposited in a crystalline state, when the solution, containing but little acid, is allowed to stand. By calcination they are freed from organic matter. Ultimately there remains a saline mass, containing chloride of calcium, chloride of ammonium, and perhaps some traces of other matters yet to be ascertained.

The ingredients of ox-gallstones according to analyses upon the above plan, are the following: Bile, a residue of the fluid in which the concretions are formed. Cholochrome, cholic and choloidic acids, cholesterine, a sulphate in some cases, phosphates of lime and magnesia, carbonates of the same, and some ammonia-compounds, possibly a sulphate.*

Analysis of Putrid Ox Bile.

It is necessary to separate some of the white granules from the fluid, in order to show by combustion and treatment with acidulated ether, that they contain phosphate and palmitate or stearate of lime. The free fatty acid forms an emulsion on boiling with phosphate of soda.

The principal step in the analysis of this fluid, is the filtration and separation of the deposit. A bag of twilled calico is best used for that purpose. When the fluid has percolated, the smeary deposit in the bag must be kneaded with cold water, as otherwise it is impossible to wash it. When well washed, it is mixed with boiling alcohol, and boiled with it for some time; it is then again put in the washed calico bag. The filtrate on cooling deposits a large quantity of crystallized cholic acid. The mother-liquor on evaporation yields little cholic, and some choloidic acid. That part of the deposit which boiling alcohol did not dissolve, is well washed with alcohol, and extracted with a boiling solution of carbonate of potassa. This solution takes up the whole of the colouring matter, cholophaeine, and leaves behind a white mass of coagulated mucus, mixed with greenish crystals of phosphate of lime, which are separated by levigation. From the soda-solution, the cholochrome is obtained as the green modification, *cholochloine,* by precipitation with hydrochloric acid.

The deposit therefore is made up of stearate and palmitate of lime, cholic and choloidic acid, cholochrome, phosphate of lime in crystals, and mucus.

The port-wine-coloured fluid part of the bile is treated with sulphuric acid in slight excess :- a large quantity of choloidic acid is then precipitated as a pitchy mass, which is easily soluble in warm alcohol, and contains but little cholic acid, deposited in crystalline granules after long standing of the alcoholic solution. The excess of sulphuric acid is removed, and any free acid neutralized by boiling the fluid residue with carbonate of baryta. When evaporated, this solution deposits resinous cholic acid (which does not decompose carbonate of baryta) to be extracted by alcohol. The alcohol causes a crystallization on standing with the fluid. The crystals consist of sulphate of soda, phosphate of soda, and taurine, to be separated mechanically, and in the ultimate mother-liquor of the decrystallized substances, some triple-phosphate is obtained, as also some chloride of ammonium, to be obtained pure by sublimation. The alcohol retains the acetate and valerate of ammonia, which salts, after evaporation of the alcohol, yield their acids on distillation with sulphuric acid. The addition of this latter acid still precipitates some resinous biliary matters.

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* I may here allude to the discovery of sulphide of ammonium, which Lehmann states to have made, in the bile of a boy.

The fluid part of putrid bile therefore contains choloidate of soda, a little cholate, a red colouring matter, perhaps cholochromic acid, taurine, valerate and acetate of ammonia, phosphate of soda, chloride of ammonium, and some other as yet undetermined matters.

Putrefaction and Analysis of Human Bile.

As human bile can only be obtained in quantity from persons who have died from disease, it will not easily afford the materials with which to repeat the experiments instituted with ox-bile, which is fresh, healthy, and normal. Human bile promiscuously collected in the dead-house, even allowing it to contain the normal ingredients, is mostly vitiated by a large amount of albumen, which enters the gall-bladder by endosmosis during the interval between death and obduction. This albumen coagulates in part during evaporation of such bile on the water-bath, another part remaining dissolved. If then such bile be subjected to putrefaction, the process takes place under different conditions, and yields therefore different results. This difference mainly consists in the circumstance, that the alkaline products of decomposition of albumen, either neutralize the acid products of the decomposition of bile, which would precipitate insoluble compounds, or dissolve them again should they have been precipitated. Deducting the products of the putrefaction of albumen, the products of the putrefaction of the bile itself are the same as those obtained from ox-bile, although they are in a different form. Human bile is mostly neutral. When dissolved in alcohol, it parts with the mucus and albumen, and the filtrate, after evaporation of the alcohol, leaves a residue, which is entirely soluble in water, and such solution is neutral and not precipitated by oxalic or acetic acid. Sometimes however human bile exhibits an acid reaction; this on similar treatment with alcohol, and re-solution in water of the residue, yields a plastery precipitate of choloidic acid. When complete precipitation has been effected, the filtrate evaporated, and the concentrated fluid treated with alcohol, prismatic crystals of taurine are sometimes obtained. The solution always yields ammonia.

Human bile, which has been allowed to putrefy in a stoppered bottle, emits a horrible odour, is of a reddish brown colour, and apart from the deposit perfectly clear: it has an acid reaction. With acetic acid, it becomes troubled, and deposits a resinous precipitate; but the supernatant fluid remains thick, and does not become clear even on boiling and standing; the addition of hot alcohol resolves the turbidity.

XI.—*On some Derivatives from the Olefines.*

By Frederick Guthrie.

IV.

A considerable number of the substances whose formation and properties I have had the honour of describing to this Society in Memoirs I, II, and III, are non-volatile and uncrystallizable liquids. Hence, with regard to them, the two so-frequently adopted criteria of homogeneity are inapplicable; viz., constancy of boiling point and crystalline form. Although this want is shared by a vast number of bodies, both organic and inorganic—solid, liquid, and gaseous,—whose homogeniety is never called into question, yet additional evidence in this direction is not superfluous.

A method peculiarly applicable in such cases, is that of fractional solution. It has been already successfully employed in determining the homogeneity of gases; and may be thus proposed. "When a solvent has partly dissolved a body, and the entire body has the same composition as either of the parts (dissolved or undissolved), or if the latter have the same composition as one another, then the original substance is simple or homogeneous."

No mixture can show this property unless its constituents are isomers or polymers of one another. The law itself enjoys, of course, nearly the same amount of truth as the proposition that no two substances are soluble to exactly the same extent, in the same medium, under the same conditions, unless the solubility of both be infinite.

The inverse of the law is untrue to the extent that solution may effect decomposition.

The substances which I have submitted to this test are the two of the substances previously described, which seemed most prolific of derivatives; viz.,

*Bisulphochloride of ethylene $C_4H_4S_2Cl$.
*Bisulphochloride of amylene $C_{10}H_{10}S_2Cl$.

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* M. Wurz (Répertoire de Chimie pure, ii, 337), in noticing these bodies and the two

$$\begin{array}{l} C_4H_4S_2Cl_2. \\ C_{10}H_{10}S_2Cl_2. \end{array}$$

remarks:—

"SCl_2, corresponding to SO_2, being diatomic, it follows that SCl_2-Cl; that is, SCl, ought to be monatomic. Nevertheless, it is to be observed, that the constitution of these bodies may be regarded in another manner, by supposing them to contain the diatomic groups,—

Sulphide of ethylene $(C_4H_4S_2)''$ and
Sulphide of amylene $(C_{10}H_{10}S_2)''$,

corresponding to the oxides. These groups, on combining with 2 atoms of chlorine, form the two following chlorides:—

Dichloride of sulphethylene $(C_4H_4S_2)''Cl_2$.
Dichloride of sulphamylene $(C_{10}H_{10}S_2)''Cl_2$.

"As for the chloride $C_{10}H_{10}S_2Cl$, we double its equivalent, representing its constitution by the formula,—

$$\left.\begin{array}{l} C_{10}H_{10}S_2 \\ C_{10}H_{10}S_2 \end{array}\right\}''Cl_2.$$

"It is known that 2 atoms of oxide of ethylene may unite, in order to combine with 1 atom of water. Hence, it is not extraordinary that 2 atoms of sulphide of amylene should join together in order to combine with 2 atoms of chlorine. If this way of looking at the matter is exact, we should represent the constitution of the oxide of disulphamylene and that of the hydrate of the oxide of disulphamylene by the formulæ—

$$\text{Oxide of sulphamylene } \left.\begin{array}{l} C_{10}H_{10}S_2 \\ C_{10}H_{10}S_2 \end{array}\right\}''O_2.$$

The method was applied as follows:—A few grammes of the bisulphochloride of ethylene were warmed, with alcohol of about 85°, until nearly half dissolved. The alcoholic solution was then poured off, and the alcohol removed by evaporation on a water-bath, and washing with water. The product, after drying in *vacuo* over sulphuric acid, gave the results—

I. 0·4436 gave 25·27%C, and 4·36H.
II. 0·4280 gave 33·88%S.
III. 0·2838 gave 36·00%Cl.

Comparing this with the analysis given before of the entire substance, we find,—

Hydrate of sulphamylene $\left.\begin{array}{c}C_{10}H_{10}S_2\\C_{10}H_{10}S_2\\H_2\end{array}\right\}''O_4$.

In reply, I would observe:—

1. That SCl_2 has not yet been formed; and that therefore speculations as to what its "atomicity" might be, are premature. Still more so must considerations be as to the effect which the withdrawal of chlorine would have on the hypothetical atomicity of this hypothetical body.

2. That, in such bodies as

$$C_{10}H_{10}S_2Cl_2,$$

it seems preferable to suppose that the halogens are arranged in two "monatomic' groups, than to imagine, with M. Wurz, that there are two stages of saturation, each stage being a biatomic one. This, applied to glycols would give,—

$$C_nH_n\begin{array}{c}HO_2\\HO_2\end{array}, \text{ instead of } \left\{(C_nH_n)''\,O_2\right\}''2HO, \text{ \&c.}$$

3. Concerning the bodies,

$$C_nH_nS_2Cl.$$

I admit, in regard to some of their reactions, we have reason (neither more nor less) to double their formulæ than to double the formulæ of the ethers. But, to write the hydrated oxide of bisulphamylene,

$$\left.\begin{array}{c}C_{10}H_{10}S_2\\C_{10}H_{10}S_2\\H_2\end{array}\right\}''O_4, \text{ instead of } C_{10}H_{10}S_2O,HO, \text{ or } C_{10}H_{10}\begin{array}{c}S_2\\HO_2\end{array},$$

is, I think, a useless complication. It does not represent the formation or properties of the body more clearly than the older formulæ; and moreover involves the idea of a "mixed type," which I have never been able to understand. But I must again insist here upon the uselessness of seeking to establish *the* formula of a body;—if formulæ of bodies at chemical rest are to express their potential recompositions. (See I.)

	$C_4H_4S_2Cl$ requires	Entire Substance	Dissolved Portion.
C	= 25·13	25·93	25·27
H	= 4·19	4·32	4·36
S	= 33·51	33·47	33·88
Cl	= 37·17	36·29	36·00
	100·00	100·01	99·51

About the same quantity of the bisulphochloride of amylene was treated in exactly the same manner. The dissolved portion, on analysis, gave the following results:—

I. 0·3934 grm. gave 23·81%S.
II. 0·2677 ,, gave 25·66%Cl.

Whence, comparing, as before, with the composition of the whole substance, we have,—

	$C_{10}H_{10}S_2Cl$ requires	Entire Substance.	Dissolved Portion.
C	= 43·64	43·80	,,
H	= 7·27	7·47	,,
S	= 23·27	23·93	23·81
Cl	= 25·82	24·73	25·66
	100·00	99·93	

Hence, it appears that, in both cases, the entire substance has virtually the same percentage composition as the dissolved portion; and accordingly, under the limitations above specified, the homogeneity of both bodies is established.

We have already seen the curious relation existing between the bisulphochloride of chlorethylene and the bisulphide of ethyl, in regard to the action on both of chlorine. The product in either case is the chlorosulphide of bichlorethylene or the sulphide of terchlorethyl.

$$C_4\left.\begin{matrix}H_2\\Cl_2\end{matrix}\right\}SCl \quad \text{or} \quad C_4\left.\begin{matrix}H_2\\Cl_3\end{matrix}\right\}S.$$

This identity of product extends also to the bisulphochloride of ethylene. If a few grammes of the bisulphochloride of ethylene be exposed to a current of dry chlorine, the action being carried on for a few hours and assisted at last by the heat of a water-bath, a product is obtained, which after expulsion of the excess of chlorine by a current of carbonic acid, showed the following composition:—

I. 0·3824 grm. gave 70·69 % Cl.
II. 0·4380 grm. gave 10·63 % S.

The sulphide of terchlorethylene requires

71·73 % Chlorine,
10·63 % Sulphur.

So that the action of chlorine is to convert the bisulphochloride of ethylene, into the sulphide of terchlorethyl. *Towards chlorine,* therefore, bodies of the form

$$C_nH_nS_2\,Cl,$$

behave like sulphides of chloriferous radicles

$$C_n\left.\begin{matrix}H_n\\ Cl\end{matrix}\right\}S_2$$

inasmuch as the bisulphides of the radicles C_nH_{n+1}, give rise to the same products.

On treating $C_{10}H_{10}S_2Cl$ with oxide of lead, or with hydrate of potash, we have already seen the chlorine replaced by O and by HO_2. Doubtless $C_4H_4S_2\,Cl$, would give rise to $C_4H_4S_2O$, on treatment with PbO. As yet I have only examined the action of hydrate of potash upon $C_4H_4S_2\,Cl$. If $C_4H_4S_2\,Cl$, and KOHO, be both in alcoholic solution, the reaction between them on slightly warming is both immediate and complete. The KOHO being employed in slight excess, and the filtrate from the precipitated KCl having been freed from alcohol by evaporation and washing with water, the hydrated bisulphoxide of amylene is obtained pure.

On analysis:

I. 0·4333 gave 31·33 % C, and 6·67 % H.
II. 0·2984 gave 42·26 % S.

	$C_4H_4S_2OHO$ requires	I.	II.
C =	31·17	31·33	„
H =	6·49	6·67	„
S =	41·56	„	42·26
O =	20·78	„	„
	100·00		

The hydrate of bisulphoxide of amylene is a yellowish liquid of curious smell; like the body from which it is derived, it acts violently upon the mucous membrance. It dissolves in alcohol and ether, but is insoluble in water.

Further transformations intimately connected with the above, and with others previously described, are afforded by the replacement of the chlorine in

$$C_{10}H_{10}S_2\,Cl,$$

by cyanogen and sulphocyanogen. The method used in both cases, is similar to that employed for the oxygen and peroxide of hydrogen replacements, viz: digestion of the $C_{10}H_{10}S_2\,Cl$ with cyanide or sulphocyanide of potassium respectively, in alcoholic solution. The reaction is very neat. The precipitated chloride of potassium having been separated by filtration, the filtrate is evaporated on a water-bath, washed with water, and dried over sulphuric acid *in vacuo*.

Both products are liquids which can scarcely be distinguished by smell or other physical property. They have however evidently different densities. The first gave on analysis:

I. 0·2432 gave 55·65 % C, and 7·60 % H.
II. 0·3881 gave 24·66 % S.

$C_{10}H_{10}S_2Cy$ requires			I.	II.
C	=	56·25	55·65	,,
H	=	7·81	7·60	,,
S	=	25·00	,,	24·66
N	=	10·94	,,	,,
		100·00		

The specific gravity of this body is 1·07 at 13° C. Since there can be little doubt but that the sulphur and cyanogen in this substance are not in the same relation as in the sulphocyanides (for if so, S_4Cy_2 would be required to saturate $C_{10}H_{10}$), it is advisable to call the above body the *bithiocyanide* of amylene, rather than the "sulphocyanide" or "bisulphocyanide."

The product obtained by the action of the sulphocyanide of potassium upon the bisulphochloride of amylene, gave the following results on analysis:

I. 0·2336 gave 44·46 C, and 6·54 H.
II. 0·3768 gave 39·32 S.

$C_{10}H_{10}S_2S_2Cy$ requires			I.	II.
C	=	45·00	44·46	„
H	=	6·25	6·54	„
S	=	40·00	„	39·32
N	=	8·75	„	„
		100·00		

The specific gravity of this body at 13°C is 1·16. The least ambiguous name which can be given to it is, perhaps, the *bithio-bithiocyanide* of amylene.

If we now compare the above and previously described behaviours of the bodies $C_4H_4S_2Cl$ and $C_{10}H_{10}S_2Cl$, with that of the halide of a radicle of the form

$$C_nH_{n+1}X,$$

we must at once admit the parallelism of the recompositions in the two cases, and therewith admit that bodies of the form

$$C_nH_nS_2Cl,$$

behave like the chlorides of the form

$$C_nH_{n+1}Cl,$$

towards oxides, hydrated oxides, cyanides, and sulphocyanides.

$$\left.\begin{array}{lll} C_nH_{n+1}X + MO & = C_nH_{n+1}O & + MX \\ C_nH_nS_2Cl + MO & = C_nH_nS_2O & + MCl \end{array}\right\}$$

$$\left.\begin{array}{lll} C_nH_{n+1}X + MHO_2 & = C_nH_{n+1}HO_2 & + MX \\ C_nH_nS_2Cl + MHO_2 & = C_nH_nS_2HO_2 & + MCl \end{array}\right\}$$

$$\left.\begin{array}{lll} C_nH_{n+1}X + MCy & = C_nH_{n+1}Cy & + MX \\ C_nH_nS_2Cl + MCy & = C_nH_nS_2Cy & + MCl \end{array}\right\}$$

$$\left.\begin{array}{lll} C_nH_{n+1}X + MS_2Cy & = C_nH_{n+1}S_2Cy & + MX \\ C_nH_nS_2Cl + MS_2Cy & = C_nH_nS_2S_2Cy & + MCl \end{array}\right\}$$

Hence the rational formula of

$$C_nH_nS_2Cl.$$

towards oxides, hydrated oxides, etc., may be written

$$C_n\left.\begin{matrix}H_n\\S_2\end{matrix}\right\} Cl,$$

wherein we have the *chloride of a sulphuriferous radicle:* for in presence of these bodies, the sulphur and hydrocarbon remain together. We here then see a prominent example of the variations in the re-agent producing a corresponding variation in the rational formula.

According to this view, the bodies

$$C_nH_nS_2O$$
$$\text{and } C_nH_nS_2HO_2,$$

represent an ether and an alcohol. An additional argument for considering $C_{10}H_{10}S_1HO_2$ as an alcohol, will be found in the fact, that on dropping it into a large excess of strong sulphuric acid, which is kept cold, a conjugate acid is produced, having a soluble baryta-salt. This acid will be described subsequently. Again it would appear from a few experiments performed in this direction, that the peroxide of acetyl may replace the chlorine in $C_{10}H_{10}S_2Cl$, by the action of acetate of potash, the acetate of bisulphamylene being produced:

$$C_{10}H_{10}S_2OC_4H_3O_3 \text{ or } C_{10}H_{10}\begin{matrix}S_2\\C_4H_3O_4\end{matrix}$$

a body which is an analogue of acetic ether. Such derivatives must for the present be reserved.

The body $C_{10}H_{10}S_2Cl$, being thus prolific, it becomes important to examine the formation and properties of the bodies formed by the union of amylene with the separate halogens S and Cl, viz:

$$C_{10}H_{10}S_2$$
$$\text{and } C_{10}H_{10}Cl_2$$

The first of these bodies, or the bisulphide of amylene, is easily obtained by the direct reduction of $C_{10}H_{10}S_2Cl$, by means of metallic zinc. Nascent hydrogen, which was at first tried, effects too profound a reduction, by withdrawing a portion of the sulphur. To prepare $C_{10}H_{10}S_2$, an ounce or two of $C_{10}H_{10}S_2Cl$ is dissolved in alcohol, and boiled for some hours with granulated zinc, the alcohol being condensed and allowed to flow back. The greater quantity of the alcohol is then distilled off, and the residue washed with water. A colourless liquid product collects on the surface of the water, which after washing and drying over chloride of calcium, may be rectified. It boils constantly at about 200°C.

1. 0·8012 gave 30·60 % S.
II. 0·2833 gave 58·32 % C, and 10·26 H.
III. 0·3270 gave 58·26 % C, and 10·24 H.

		$C_{10}H_{10}S_2$ requires	I.	II.	III.	
C	=	58·82	,,	58·32	58·26	58·29
H	=	9·80	,,	10·26	10·24	10·25
S	=	31·38	30·60	,,	,,	30·60
		100·00				99·14

The specific gravity of the bisulphide of amylene is 0·907 at 13°C.

Considerable difficulty attends the formation of bichloride of amylene.

$$C_{10}H_{10}Cl_2.$$

Amylene absorbs chlorine with the greatest eagerness; but when the two are brought together alone, as also when cold chlorine-water acts upon amylene, floating on its surface, large quantities of hydrochloric acid are formed, which points to the occurrence of some chlorhydrogen replacement. The formation of Dutch liquid by the action of pentachloride of antimony upon ethylene, suggested the possible formation of

$$C_{10}H_{10}Cl_2$$

by an analogous process.

Pentachloride of phosphorus was finely pounded and treated with perfectly dry amylene. No hydrochloric acid escaped, a few degrees of heat were evolved, and the whole became nearly dry. After having stood for twelve hours, the mass was placed in a basin and floated on water. At the end of another twelve hours, two layers were found, the lower consisting of phosphoric, and as experiment showed, phosphorous acid and hydrochloric acid,—the upper of bichloride of amylene. From the fact that the amylene and pentachloride of phosphorus produced in the first instance a solid, it would appear that the complementary PCl_3 re-united with the amylene to form the unstable body

$$C_{10}H_{10}PCl_3,$$

which subsequently underwent decomposition. After washing with water and drying, the upper layer was rectified. A product was thus obtained, which boiled at 141° – 147°C. On analysis:

I. 0·2866 gave 42·22 % C, and 7·40 % H.
II. 0·4279 gave 50·88 % Cl.

		$C_{10}H_{10}Cl_2$ requires	I.	II.
C	=	42·55	42·22	,,
H	=	7·09	7·40	,,
Cl	=	50·36	,,	50·88
		100·00		100·50

At 9° C. bichloride of amylene has the specific gravity 1·058.

It is not improbable that bichloride of amylene may give rise to bicyanide of amylene, on treatment with cyanide of potassium. Bicyanide of amylene may however be prepared in another and very singular manner.

It will be remembered that the gas NO_4 unites directly with amylene to form the body $C_{10}H_{10}.2NO_4$ (see III). This fact was used to support the view of NO_4 being a true halogen. The same conclusion is also suggested by the behaviour of $C_{10}H_{10}.2NO_4$ towards cyanide of potassium. If $C_{10}H_{10}.2NO_4$ be dissolved in alcohol at a gentle heat,[*] and added to an alcoholic solution of cyanide of potassium, an immediate precipitate is produced, which, after washing with alcohol and drying, gives a precipitate with nitrate of silver, soluble in nitric acid, and which, on treatment with sulphuric acid, gives an amount of sulphate of potash corresponding to the nitrite of potash (nitroxide of potassium). The alcoholic solution from the nitrite of potash is evaporated on a water bath, at about 60°C, until the greater portion of the alcohol is expelled. The residue is then repeatedly washed with small quantities of water, and dried over sulphuric acid in *vacuo*. The composition of the liquid product was found by analysis to be as follows:—

0·2760 gave 9·16 % of H.
0·3500 gave 9·16 % of H, and 51·26 of C.
0·3079 gave 16·00 % of N.

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[*] An alcoholic solution of $C_{10}H_{10}2NO_4$ is decomposed on boiling. Chloroform dissolves $C_{10}H_{10}$ $2NO_4$ abundantly, as also does glacial acetic acid. Strong sulphuric acid instantly decomposes it.

$C_{10}H_{10}Cy_2 + 5HO$ requires			I.	II.	III.
C	=	50·30	,,	51·26	,,
H	=	8·98	9·16	9·16	,,
N	=	16·77	,,	,,	16·00
		76·05			76·42

The body according to this analysis, is the pentahydrate of bicyanide of amylene. The water attached to the cyanide is to be compared to water of crystallization. It is given off on heating the hydrate, but remains combined when the hydrate is exposed for any time over sulphuric acid. It may be sufficient here to notice—(1) That five equivalents of water would be essential to the conversion of the cyanide of amylene into pimelate of potash by the action of caustic potash. (2) That my few experiments to prepare pimelate of potash from the cyanide have not been successful.

The binitroxide of amylene appears also to exchange its NO_4 for O, HO_2 S, and S_2Cy. Most of these bodies will probably be soon described by those chemists who are engaged in researches on the diatomic alcohols.*

A body intimately connected, on the one hand, with $C_{10}H_{10}2NO_4$, and, on the other, with the chlorine-derivatives of $C_{10}H_{10}S_2Cl$, is the product of the action of $HO.NO_5$ upon $C_{10}H_{10}S_2Cl$.

On warming $HO.NO_5$ with $C_{10}H_{10}S_2Cl$, a tempestuous, and, in some respects, complicated, reaction is established. One phase of the reaction results in the formation of the products,

$$SO_3,\ HCl \text{ and } C_2HO_4.$$

showing that a part of the $C_{10}H_{10}S_2Cl$ has suffered complete disorganisation. Moreover, a copulated sulphuric acid is formed, which has a soluble baryta-salt, but has not been further examined. The other, and more easily applicable reaction, is the formation of

$$C_{10}\begin{matrix}H_9S\\NO_4NO_4\end{matrix},$$

or, the nitrosulphide of nitroxamylene.

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* Dr. Simpson's preparation of cyanide of ethylene, and thence of succinate of potash, will, I expect, on publication of his analyses, throw light on this subject.

It is this body which appears in the distillate when $C_{10}H_{10}S_2Cl$ is warmed in a retort with $HO.NO_5$, as a heavy liquid of green colour, insoluble in water. After washing with water and drying, it is pure.

grms.
0·2579 gave 34·82%C and 4·82%H.
0·2620 gave 34·26%C and 5·25%H.
0·1838 gave 9·39%S

	$C_{10}H_9S2NO_4$ requires.	I.		
C =	33·89	34·82	34·26	„
H =	5·08	4·82	5·25	„
S =	9·04	„	„	9·39

The nitroxisulphide of nitroxamylene is soluble in ether and alcohol, and suffers, apparently, very easy reduction by sulphide of ammonium.

Before leaving this part of the subject, it may be in place to offer a view connecting the two nitroxiolefines described with some known bodies. Such connection at once appears on looking at the following list, which might be much extended.

	Example.
C_nH_n, or $C_nH_n\{C_nH_n$	Olefiant gas.
$C_nH_n\left\{\begin{matrix}C_nH_{n+1}\\H\end{matrix}\right.$	Ethyl.
$C_nH_n\left\{\begin{matrix}Z_n\\H\end{matrix}\right.$	Zinc-ethyl.
$C_nH_n\left\{\begin{matrix}C_mH_{m+1}\\H\end{matrix}\right.$	Ethyl-amyl.
$C_nH_n\left\{\begin{matrix}H\\H\end{matrix}\right.$	Hydride of ethyl.
$C_nH_n\left\{\begin{matrix}H\\Cl\end{matrix}\right.$	Chloride of ethyl.
$C_nH_n\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	Dutch liquid.
$C_nH_n\left\{\begin{matrix}H\\O\end{matrix}\right.$	Ether.

$C_nH_n\left\{\begin{matrix}H\\HO_2\end{matrix}\right.$	Alcohol.
$C_nH_n\left\{\begin{matrix}O\\O\end{matrix}\right.$	Ethylenic ether.
$C_nH_n\left\{\begin{matrix}HO_2\\HO_2\end{matrix}\right.$	Glycol.
$C_nH_n\left\{\begin{matrix}NO_4\\NO_4\end{matrix}\right.$	Binitroxide of amylene.
$C_n\begin{matrix}H_{n-1}\\NO_4\end{matrix}\left\{\begin{matrix}S\\NO_4\end{matrix}\right.$	Nitroxisulphide of nitroxamylene.
$C_nH_n\left\{\begin{matrix}SO_3\\SO_3\end{matrix}\right.$	"Sulphate of carbonyl."
$C_nH_n\left\{\begin{matrix}H\\NO_4\end{matrix}\right.$	Glycocine.

To which might be added the much-formulized acid series:—

$C_nH_{n-2}\left\{\begin{matrix}HO_2\\HO_2\end{matrix}\right.$	Hydrated acetic acid.
$C_nH_{n-2}\left\{\begin{matrix}HO_2\\O\end{matrix}\right.$	Acetic anhydride.

A series such as the above may assert a claim rather as a device for classification than as a method of accomplishing what most formulæ profess to perform, viz., an index to molecular arrangement.

To many of what are called homologous series, methylene plays the same part chemically as the common difference plays in an arithmetic series. Hence the question forces itself upon us: Is it possible, by means of the successive chemical additions of methylene, to advance from an inferior to any superior term of such a homologous series?

The doubt as to the existence of methylene, and even, in the eyes of some, as to the possibility of its existence, puts a practical end to this question at present.

A moment's consideration shows that the successive formation of all higher terms could be effected by means of ethylene, provided *two* consecutive homologous terms were taken, that is, terms differing by methylene.

Further, by means of propylene, we could effect the same purpose, provided that *three* consecutive homologous terms were at our disposal to begin with. And so *mutatis mutandis* for the other olefines.

The suggestion as to the possibility of this method of building up was already given in Memoir I, wherein the action of zinc-ethyl upon $C_{10}H_{10}S_2Cl$ was suggested. The subsequent experiments which have been described as to the easy replacement of the Cl in $C_{10}H_{10}S_2Cl$ by other halogens only confirmed this idea. In zinc-ethyl, as far as it consists of zinc and ethyl, the ethyl is the halogen. Can, then, the ethyl from zinc-ethyl be made to replace the chlorine $C_nH_nS_2Cl$? and what relation will the body thus produced bear to the bisulphide of œnanthyl?

$$C_{10}H_{10}S_2C_4H_5 \quad , \quad C_{14}H_{15}S_2?$$

If an excess of ethereal solution of zinc-ethyl (as it comes from the digester) be allowed to fall upon the bisulphochloride of amylene, considerable heat is developed. It is best to allow the heat to moderate itself by the evaporation of the ether, and not to cool artificially. Two layers are formed. These are treated separately with water, the oil which floats on the surface is taken off, and the solid body (oxide of zinc) is exhausted with alcohol. The alcoholic solution and the oil are mixed, freed from alcohol by gentle evaporation, washed with water, dried and rectified. The product boils almost constantly at about 240°–250°C. It gave, on analysis,

0·2730 gave 65·31%C and 11·22H.
0·4152 gave 65·4%2C and 11·26H.
0·4186 gave 23·72%S

	$C_{14}H_{15}S_2$ requires	I.	II.	III.
C	64·12	65·31	65·42	,,
H	11·46	11·22	11·26	,,
S	24·42	,,	,,	23·72
	100·00			100·32

so that the product has, in fact, the percentage-composition of bisulphide of œnanthyl.

Although I believe by this means to have found the key to the problem of the successive synthesis of ascending terms of a homologous series; it will be more generally acceptable if the above body be termed, for the present, the bisulphethide of amylene.

$$C_{10}H_{10}\left\{\begin{matrix}S_2\\C_4H_5\end{matrix}\right. .$$

An examination of the products of recomposition of this and similar bodies I reserve for a future communication.

The bodies which I have had the honour of bringing before the notice of the Society in this and previous Memoirs, are the following:—

From Ethylene.

$C_4H_4S_2Cl$	Bisulphochloride of ethylene.
$C_4H_4S_2Cl_2$	Bichlorosulphide of ethylene.
(α) $C_4H_2SCl_3$	Chlorosulphide of bichlorethylene.
(β) $C_4H_2SCl_3$	Sulphide of terchlorethyl.
$C_4H_4S_2HO_3$	Hydrate of bisulphoxide of ethylene.

From Amylene.

$C_{10}H_{10}S_2Cl$	Bisulphochloride of amylene.
$C_{10}H_{10}S_2Cl_2$	Bichlorosulphide of amylene.
$C_{10}H_7SCl_4$	Chlorosulphide of terchloramylene.
$C_{10}H_{10}S_2O$	Bisulphoxide of amylene.
$C_{10}H_{10}S_2HO_2$	Hydrated bisulphoxide of amylene.
$C_{10}H_9S_2$	Bisulphide of fusyl.
$C_{10}H_{10}S_2$	Bisulphide of amylene.
$C_{10}H_{10}Cl_2$	Bichloride of amylene.
$C_{10}H_{10}Cy_2+5HO$	Penthydrated bicyanide of amylene.
$C_{10}H_{10}S_2Cy$	Bithiocyanide of amylene.
$C_{10}H_{10}S_4Cy$	Bithiosulphocyanide of amylene.
$C_{10}H_{10}.2(NO_4)$	Binitroxide of amylene.
$C_{10}H_9S.2(NO_4)$	Nitroxisulphide of nitroxamylene.
$C_{10}H_{10}S_2C_4H_5$	Bisulphide of œnanthyl.

The above are, of course, merely the equivalent formulæ. The formulæ of all these compounds are on the type

$$C_nH_n{}^{X}_{X}.$$

XII.—*On the amount of Water displaced from the Hydrates of Potash, Soda, and Baryta by Boracic and Silicic Acids.*

By Charles L. Bloxam.

In a communication which was printed in the Society's Journal of July, 1859, I described a series of experiments upon the action of boracic acid on the carbonates of the alkalies and alkaline earths at high temperatures, from which it appeared, that, at a bright-red heat, one equivalent (34·9) of that acid is capable of expelling from carbonate of potash, one equivalent (22) of carbonic acid, from carbonate of soda, two equivalents; from carbonate of lithia, two and a half equivalents; from carbonate of baryta, two and a half equivalents; and from carbonate of strontia, three equivalents of carbonic acid.

It would be inferred, from these results, that one equivalent of boracic acid is capable of combining with three equivalents (and perhaps even with more) of a basic oxide of the type MO, and that its capacity for bases could not be fully satisfied by its action upon the carbonates of the more powerful bases, on account of the energy with which they retained their carbonic acid.

It might be expected that since the water is more easily expelled from the hydrates, than the carbonic acid from the carbonates, the former would allow the boracic acid to satisfy its capacity for bases far more readily, and it might be hoped that a limit would be found to the displacing power of this acid for water.

In the experiments made to determine this question with the hydrates of potash and soda, fair specimens of the fused hydrates were heated to dull redness in a silver tray enclosed in a glass tube, through which a current of air was drawn by an aspirator, the air having traversed, before entering the tube, a wash-bottle with strong potash, a wash-bottle with oil of vitriol, a U-tube with fragments of fused potash, and a second U-tube with pumice and oil of vitriol. The composition of the hydrates fused under these circumstances until of constant weight, having been carefully determined, fresh quantities were fused in the tray and weighed in the corked tube, at intervals of ten or fifteen minutes, until their weight ceased to vary to any important extent. A weighed quantity of freshly fused boracic acid was then introduced as rapidly as possible, the tube and its contents being again weighed, in case a little water or carbonic acid should have been absorbed from the air. Heat was then gradually applied to the tube, and the boracic acid fused with the hydrate, in the current of pure and dry air, until the weight of the (corked) tube and its contents ceased to vary to any extent capable of affecting the result of the experiment. At the conclusion, the temperature was always high enough to soften the hard glass tube, an Argand gas-lamp being employed, and a hood of sheet platinum being placed over the heated part of the tube.

Since, in this way, the boracic acid was allowed to act upon the same sample of hydrated alkali, which had already been subjected to the same conditions until it ceased to lose weight, any loss which was suffered during the fusion with the boracic acid must represent the amount of water displaced from the hydrate by that acid.

In many of the experiments, a weighed chloride of calcium tube was introduced between the fusion-tube and the aspirator, and after this had ceased to gain any water from the fused hydrate alone, the boracic acid was introduced and the experiment continued until the drying tube suffered no increase of weight.

The gain of the chloride of calcium tube was found to correspond almost exactly with the loss of the fusion-tube.

Action of Boracic Acid upon Hydrate of Potash at a red heat.

A somewhat unexpected difficulty arose in the course of these experiments, from the tendency of the fused hydrate of potash to absorb oxygen when heated in a current of air.

When 50 grains of the hydrate, which had been heated to fusion in the silver tray, and maintained in fusion for half an hour in the stream of dry and pure air, were allowed to cool, and dissolved in water, 0·4 cubic inch of oxygen escaped with rapid effervescence, and grey spangles of silver separated. The loss suffered by the silver tray in the course of the experiment amounted to 0·14 grn., and the corrosion of the tray was evident, soon after the commencement of the fusion, from the appearance of lustrous spangles of silver in the clear fused hydrate.

The fused masses obtained with hydrate of potash and boracic acid effervesced very rapidly with water, from the evolution of oxygen, and allowed inky black flakes to separate, which appeared to be simply silver in a finely divided state.

In order to ascertain to what extent this absorption of oxygen would interfere with the determination of the amount of water displaced by the boracic acid, the tube containing the fused mass was heated until its weight was very nearly constant, and a weighed drying tube was then attached to the fusion-tube; on continuing the application of heat for half an hour, in a current of dry and pure air, the fusion-tube with the hydrate had lost only 0·02 grn., whilst the drying tube had gained 0·17 grn. of water, showing that the absorption of oxygen by the fused hydrate was attended by a disengagement of water. On dissolving the fused mass in water, 0·5 cubic inch of oxygen was collected, the weight of which would be 0·17 grn., so that it would have exactly counterbalanced the loss of water. Doubtless the oxygen absorbed is not exactly equal to the water expelled; but it was proved by several experiments that the difference between the two weights was not sufficient to affect the result of the experiment.

In no case of the fusion of boracic acid with hydrate of potash, was more than 0·5 cubic inch of oxygen disengaged when the mass was dissolved in water.

In order to ascertain the composition of the specimen of hydrate of potash employed, and to prove that when subjected to the conditions of the experiment, the potash remained in combination with a single equivalent of water, the following experiments were made.

1. 29·16 grns. of a good specimen of the fused hydrate were fused, in the silver tray, in a current of pure dry air, for fifteen minutes, till the hydrate began to volatilise slightly. The loss amounted to 3·56 grns. or 12·2 per cent., representing the extraneous water. On further heating for ten minutes, it gained 0·03 grn.

25·04 grns. of this fused mass, dissolved in water, and the carbonic acid determined in Fresenius and Will's apparatus, gave 0·8 grn. carbonic acid, or 3·19 per cent.

2. 27·96 grns. of the hydrate which had been fused till it ceased to lose weight, were dissolved in water, and the total amount of available alkali determined by neutralising with hydrochloric acid of known strength. The (alkaline) potash present amounted to 22·79 grns. or 81·5 per cent. Deducting from this the weight of potash required to combine with the carbonic acid, viz. 6·8 grns., there are left 74·7 grns. of potash present as hydrate, which would give 89·0 per cent. of hydrate of potash.

The solution neutralised with hydrochloric acid was evaporated to dryness, the residue ignited and weighed; it gave 36·64 grns., which contained 0·37 grn. of sulphate of potash, and 0·36 grn. of chloride of calcium, leaving 35·91 grns. of chloride of potassium, representing 22·65 grns. of potash, or 81·0 per cent. Deducting from 100 parts of the hydrate, the sum of the constituents thus determined (viz.: potash, carbonic acid, sulphate of potash, and lime), amounting to 85·24 grns., there are left 14·76 grns. to represent the water of hydration. The amount of water required by theory to combine with the 74·7 of potash present as hydrate, would be 14·3 grns.

Since the sample contained small quantities of alumina, silica, and chloride of potassium, it may fairly be concluded that one equivalent of potash was combined in the fused hydrate with one equivalent of water.

The hydrate of potash fused till it ceased to lose weight, contained therefore, in 100 parts,

Hydrate of potash	89·00
Carbonate of potash	9·99

with a little lime, alumina, sulphuric acid, silica, and chlorine.

Three experiments were made upon the action of boracic acid on the hydrate of potash, with the results exhibited in the subjoined table.

	Actual weights in grains.			Number of equivalents.[*]		
	Boracic Acid.	Hydrate of Potash[†].	Water expelled.	Boracic Acid.	Hydrate of Potash.	Water expelled.
I.	9·92	41·90	5·01	1	2·60	1·96
II.	9·28	41·69	4·75	1	2·70	1·98
III.	4·96	31·78	2·59	1	3·98	2·02

In the last experiment, the air, after leaving the tube in which the fusion was conducted, passed through a bottle containing lime-water, which gave not the least indication of the presence of carbonic acid.

The mean of the last two experiments would give exactly two equivalents (18) of water displaced by one equivalent (34·9) of boracic acid from an excess of hydrate of potash.

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[*] Equivalent of boracic acid = 34·9; hydrate of potash = 47; water = 9.

[†] Calculated from the result of the preliminary analysis.

Action of Boracic Acid upon Hydrate of Soda at a red heat.

Hydrate of soda attacked the silver tray very slightly, its weight, in some experiments, not having perceptibly diminished; and the fused mass evolved hardly a trace of gas when dissolved in water.

The sample of hydrate of soda employed, when fused till its weight was constant, lost 1·27 per cent. of extraneous water.

The hydrate thus freed from water, was analysed, as in the case of hydrate of potash, and was found to contain, in 100 parts,

Hydrate of soda	90·41
Carbonate of soda	4·02

with a little alumina, silica, lime, chlorine, and sulphuric acid.

The subjoined table exhibits the results of three experiments upon the action of boracic acid on the hydrate of soda.

	Actual weights in grains.			Number of equivalents[*].		
	Boracic Acid.	Hydrate of Soda.[†]	Water expelled.	Boracic Acid.	Hydrate of Soda.	Water expelled.
I.	4·89	81·91	3·77	1	5·6	2·98
II.	4·46	35·78	3·43	1	7·0	2·98
III.[‡]	2·67	„	2·10	1	„	3·04

The mean of these experiments would give exactly three equivalents (27) of water displaced by one equivalent (34·9) of boracic acid from an excess of hydrate of soda.

Action of Boracic Acid upon Hydrate of Baryta at a red heat.

Since it was proved by experiments described in a former communication[‡] that hydrate of baryta when fused in a silver crucible till of constant weight is represented by the formula BaO.HO, the experiments upon the quantity of water displaced from it by boracic acid were made in a closed silver crucible.

Crystallised hydrate of baryta, the purity of which had been ascertained by a quantitative analysis, was effloresced in vacuo over oil of vitriol, until it was converted into the compound BaO.HO + Aq.[§]. The proportion of water having been verified by direct experiment, a weighed quantity of the hydrate was rapidly and intimately mixed with a weighed quantity of pure boracic acid dried at 212° Fah., which had been previously shown to have the composition $HO.BO_3$.

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[*] Equivalent of soda = 31

[†] Calculated from the result of the preliminary analysis.

[‡] A fresh quantity of boracic acid was added to the fused mass in II, and the experiment continued.

[§] Quarterly Journal Chem. Soc. April, 1860.

The crucible was then covered and heated until it ceased to lose weight. By subtracting from the loss of weight suffered by the contents of the crucible, the weight of water known to be expelled by heat from the effloresced hydrates of baryta and boracic acid, the amount of water really displaced from the hydrate of baryta by the boracic acid was inferred.

In the following table, the results of four experiments of this description are recorded.

	Actual weight in grains.			Number of equivalents*.		
	Boracic Acid ($HO.BO_3$).	Hydrate of Baryta ($BaO\ HO + Aq.$)	Water expelled.	Boracic Acid.	Hydrate of Baryta.	Water expelled†.
I.	3 17	27·36	5·36	1	4·00	2·92
II.	3·00	22·93	4·86	1	3·55	3·12
III.	2·51	21·60	4·17	1	4·00	3 11
IV.	2·96	25·47	4·87	1	4·00	3 03

From the mean of these experiments, it appears that almost exactly three (3·045) equivalents (27) of water are displaced by one equivalent (34·9) of boracic acid from an excess of hydrate of baryta.

If the equivalent of boracic acid be taken as 34·9, it displaces, from hydrate of potash, two equivalents, and from the hydrates of soda and baryta, three equivalents of water. Now, it was found in the experiments cited above, that one equivalent of boracic acid displaced only two and a half equivalents of carbonic acid from the carbonate of baryta, though it displaced three equivalents from the carbonate of strontia, which stands in the same position with respect to the carbonates, as hydrate of baryta does to the hydrates, that is, the next in the series of carbonates (carbonate of lime) is decomposible by heat alone, just as hydrate of strontia (the next in the series of hydrates).

If it be granted that the water in hydrate of baryta is more easily displaced than that in hydrate of soda, it follows that since boracic acid displaces no more water from the former than from the latter, its capacity for bases must be satisfied by the three equivalents of soda or baryta with which it then combines, as by the three equivalents of strontia with which it combined when heated with the carbonate.

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* Equivalent of baryta = 76 5.

† After deducting that due to the materials.

If the number 34·9 be retained for the equivalent of boracic acid, it must therefore be regarded as a tribasic acid; a view which may be thought to receive some support from the following considerations.

Boracic ether is represented, upon the ethyl hypothesis, as $3C_4H_5O. BO_3$, and its analogues in the methyl and amyl series have a similar composition. Crystallised boracic acid has the formula $3HO.BO_3$. Borate of magnesia, obtained by Rammelsberg by boiling a solution of borax with sulphate of magnesia, had the composition $3MgO. BO_3$. Octohedral borax, and common borax dried at 212° F., have the composition $NaO.2BO_3 + 5HO$, which may be represented as a tribasic salt if the water be considered to play the part of a base.

The biborate of potash, according to Laurent, has a similar composition $KO.2BO_3 + 5HO$. A terborate of potash, obtained by Laurent, had the composition $KO.3BO_3 + 8HO$, which would also be a tribasic salt if the water were admitted into the formula.

The tendency of boracic acid to form acid salts and double salts, is not observed in acids which are undeniably monobasic.

Action of Silicic Acid upon Hydrate of Potash at a red heat.

The experiment was conducted in exactly the same manner as in the case of boracic acid. The fused mass of silicate of potash dissolved, in every case, entirely in water, with the exception of a few white lustrous flakes of silver, disengaging oxygen with rapid effervescence. The largest quantity of oxygen disengaged (from a mass containing 40 grains of hydrate of potash, which had been fused for about an hour, in all) was 0·9 cub. in., which would weigh 0·31 grn., and would be at least partly compensated for (as shown by the experiment previously cited) by a corresponding displacement of water from the fused hydrate.

The annexed table contains the results of four experiments.

	Actual weights in grains.			Number of equivalents.*		
	Silicic Acid.	Hydrate of Potash†.	Water expelled.	Silicic Acid.	Hydrate of Potash.	Water expelled.
I.	4·65	31·46	2·15	1	3·6	1·54
II.	4·64	41·23	2·26	1	4·7	1·62
III.	5·20	32·17	2·44	1	3·3	1·45
IV.	4·97	31·24	2·29	1	3·3	1·53

* Equivalent of silicic acid (SiO_2) = 30.

† Calculated from the result of the preliminary analysis.

The silicic acid used in these experiments had been prepared by the fusion of sand with carbonate of soda, and carefully purified from all soluble ingredients by the usual processes.

It appears from these experiments that the proportion of water expelled increases, to a slight extent, with the proportion of hydrate of potash employed; but if the mean of experiments I, III, and IV be taken, we have almost exactly 1·5 eqs. (13·5) of water displaced by one equivalent (30) of silicic acid from an excess of hydrate of potash at a red heat*

Action of Silicic Acid upon Hydrate of Soda at a red heat.

The same specimen of silicic acid was used for these experiments, together with the hydrate of soda employed in the case of boracic acid.

	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Soda†.	Water expelled.	Silicic Acid.	Hydrate of Soda.	Water expelled.
I.	4·83	35·75	2·94	1	5·5	2·02
II.	4 91	34·04	3·03	1	5·2	2 05

These results indicate that almost exactly two equivalents (18) of water are displaced by one equivalent (30) of silicic acid from an excess of hydrate of soda at a red heat.*

Action of Silicic Acid upon Hydrate of Baryta at a red heat.

The experiments with hydrate of baryta and silicic acid were attended, as might be expected, with more difficulty, partly from the want of fusibility of the silicate of baryta, and partly from the disparity in the equivalent numbers of these bodies.

The first three experiments in the table were made in a covered silver crucible, and the fourth in the silver tray, heated in a current of dry and pure air.

In experiments II and III, the silicic acid (in II, prepared from sand, in III pure rock-crystal) was mixed with effloresced hydrate of baryta, the extraneous water having been determined by preliminary analysis, and allowed for in the calculation.

In I and IV, the hydrate of baryta was fused till it ceased to lose weight, the silicic acid then added, and the fusion continued till no further loss was perceived.

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* Col. Yorke found that 30 parts of silicic acid expelled 8·76 of water (0·97 eqs.) from hydrate of potash, and 15·7 of water (1·74 eqs.) from hydrate of soda, the fusion being effected in a deep crucible.

† Calculated from the preliminary analysis.

The fused mass, in every case, gelatinised when treated with dilute hydrochloric acid.

	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Baryta ($BaO.HO$).	Water expelled.	Silicic Acid.	Hydrate of Baryta.	Water expelled.
I.	1·97	21·30	1·09	1	3·8	1·84
II.	3·31	30·47	1·83	1	3·2	1·85
III.	3·61	30·49	1·97	1	3·0	1·82
IV.	2·85	31·78	1·61[*]	1	3·9	1·88

It may, I hope, be fairly inferred from these experiments, that one equivalent (30) of silicic acid does not displace more than two equivalents (18) of water from hydrate of baryta at a red heat.

Silicic acid then, like boracic, appears to have satisfied its capacity for bases in its action upon hydrate of soda, when it combines with two equivalents of that alkali, since it refuses to displace a larger proportion of water from the hydrate of baryta. If the formula SiO_2 (= 30) be accepted for silicic acid, it would be a bibasic acid, a conclusion to which the following considerations lend some support.

The disilicate of ethyl has the formula $2C_4H_5O.SiO_2$. The ordinary specimens of crystallised finery-cinder and of the slag from copper-smelting furnaces (melting for coarse metal), have the composition $2\,FeO.SiO_2$. It is also commonly asserted that the most fusible slag from the blast furnace is that in which the oxygen contained in the bases equals that in the silicic acid, which is the case in silicates of the bibasic type ($2MO.SiO_2$).

Berzelius obtained the salts—

$$KO.\ Al_2O_3.2SiO_2 \text{ and}$$
$$NaO.Al_2O_3.2SiO_2$$

which are obviously bibasic, since Al_2O_3 is equivalent to $3MO$.

Scheerer[†] has recently found that 30 parts of silicic acid fused with a large excess of carbonate of soda at a high temperature, expel 44 parts of carbonic acid. Col. Yorke had previously shown that 30 parts of silicic acid expelled 44 parts of carbonic acid from carbonate of lithia at a high temperature.

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[*] Increase of weight of the chloride of calcium tube. The loss of weight suffered by the fusion tube was 1·63, which would give 1·91 eqt. of water displaced by 1 eqt. of silicic acid. On the supposition that 1 eqt. of SiO_2 had displaced 2 eqs. HO, the actual weight of the water should be 1·71 grns.

[†] Ann. Ch. Pharm. cxvi. 129.

The disposition of silicic acid to form acid salts and double salts does not belong to a monobasic acid.

The formulæ of some of the chief natural silicates constituted upon a bibasic type are here given.

Villarsite	$2(2MgO.SiO_2) + Aq.$
Batrachite	$2CaO.SiO_2 + 2MgO.SiO_2$[*]
Cerite	$2CeO.SiO_2 + 2Aq.$
Bucholzite	$2Al_2O_3.3SiO_2$
Pholerite	$2Al_2O_3.3SiO_2 + Aq.$
Vesuvian	$3MO.M_2O_3.3SiO_2$[†].
Garnet	$3MO.M_2O_3.3SiO_2$
Scapolite Anorthite	$CaO.Al_2O_3.2SiO_2$
Sodalite	$3(NaO.SiO_2 + Al_2O_3.SiO_2) + NaCl.$
Zircon	$2ZrO.SiO_2$
Phenakite	$2GlO.SiO_2$
Helvine	$GlO.MnO.SiO_2$
Hydrosilicate of manganese	$2MnO.SiO_2 + 2Aq.$
Karpholite	$MnO.Al_2O_3.2SiO_2 + 2Aq.$
Electric Calamine	$2ZnO.SiO_2 + Aq.$
Hyalosiderite	$4MgO.2FeO.3SiO_2.$
Knebelite	$MnO.FeO.SiO_2$
Cyanite	$2Al_2O_3.3SiO_2$ (Klaproth).
Hisingerite	$FeO.Fe_2O_3.2SiO_2 + 6Aq.$
Olivine	$2(MgFe)O.SiO_2$

Several points of resemblance between carbon, boron, and silicon, as well as between their acids, lead many chemists to associate them as a natural group. But the atomic weights (6, 10·9, and 14) do not exhibit any such simple numerical relation as is frequently to be traced in other groups of elements presenting similar analogies.

If the group BO_3 which appears by the above experiments, to represent 3HO, be supposed really to contain 3 atoms of boracic acid, the atomic weight of the latter would be $\frac{34\cdot8}{3}$ or 11·6 and that of boron, 3·6.

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[*] According to Mitscherlich, many furnace slags, having the crystalline form of olivine have the same composition as batrachite (Gmelin).

[†] MO representing CaO, FeO, MnO, or MgO, and M_2O_3, Fe_2O_3 or Al_2O_3.

Again, if SiO_2 be supposed to represent 2 atoms of silicic acid, the atomic weight of the latter would be $\frac{30}{2}$ or 15, and that of silicon 7.

The atomic weights of the three elements would then be

Boron	3·6
Carbon	6
Silicon*	7

The atomic weight of boron added to twice that of silicon, would then give (17·6) nearly thrice that of carbon.

If boracic acid be regarded as BO_2, the atomic weight of boron would be 7·3, or almost exactly half that assigned by Berzelius to silicon (14·8).

According to this view, the numbers would be

Carbon	6
Boron	7·3
Silicon	14·8

an arrangement more in accordance with our knowledge of the gradations observed in the properties of carbonic, boracic, and silicic acids, such as their displacing power over water, their physical states, solubility, acid character, &c.

XIII.—*On some Minerals from Chile.*

By Frederick Field.

A short paper published in the Journal of this Society (Vol. xii, p. 8) on some minerals containing arsenic, sulphur, and copper from Chile, was concluded by the observation that I was then engaged in the investigation of a mineral containing sulphur, antimony, copper, and iron, with small quantities of silver, the ore being thickly sprinkled with bisulphide of iron: no specimen could be obtained pure enough for analysis. After much time had been bestowed upon this substance, no formula could be deduced, as the iron pyrites seemed to be intimately blended with the mineral itself. The discovery of the compound Cu_2S,AsS_3 analogous to the beautiful silver mineral AgS,AsS_3 rendered it very interesting to find a corresponding Cu_2S,SbS_3 to the dark antimonial silver ore AgS,SbS_3. All endeavours, however, as just observed, were unsuccessful. The pentasulphide of antimony in combination with 3 equivalents of disulphide of copper, corresponding to *Guayacanite* (the new mineral I described in the paper above referred to) which consists of pentasulphide of arsenic, with 3 equivalents of disulphide of copper, is also unknown at present.

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* If the atomic weight of silicic acid be taken, according to Berzelius, as 30·8, that of silicon, upon the above hypothesis, would be 7·2; or, if that given by Pelouze (30·2) be employed, the atom of silicon would be 7·1, almost exactly double that of boron.

Further investigations, however, led to the discovery of many singular specimens, some of which, though not altogether new to mineralogical science, may prove interesting to the Society.

Protoxide of Copper.—The combination of one equivalent of copper with one of oxygen, as a mineral production, is rather rare. The suboxide of copper so frequently encountered where the native metal prevails, appears, upon exposure to the atmosphere, or from other causes more difficult to explain to pass at once to the dicarbonate, assuming at the same time both oxygen and carbonic acid. The black earthy looking belt, which so frequently surrounds masses of ruby copper, and which is described in some works as the protoxide, contains, as far as my own experience extends, a very large proportion of sulphur, and although, not perhaps, a true definite oxysulphide, can by no means be regarded as a protoxide; in fact it contains no protoxide whatever, but is a mixture of disulphide and suboxide of copper. The black oxide of copper had only been known as existing in the Vesuvian lavas, until the great discoveries in North America, both in the valley of the Mississipi and on the borders of lake Superior, revealed this mineral in comparatively large quantities. Quite recently extensive veins of copper ore have been discovered in the extreme north of Chile (at longitude 25° S.), consisting essentially of protoxide of copper associated with carbonate of lime and a dark lustrous mineral, apparently a variety of hornblende. The ore, which has a dark brown earthy aspect, effervesces strongly upon addition of hydrochloric acid, so that at first it might be supposed to be a combination of the metal with carbonic acid; but that this is not the case is evident, upon a closer investigation of the mineral, as well as from the fact that it can be ignited to low redness, and maintained at that temperature for some little time, without suffering much diminution in weight, whereas the carbonates of copper are deprived of their carbonic acid almost instantaneously when exposed to high degrees of heat. A qualitative examination showed the presence of oxide of copper, sesquioxide of iron, carbonic acid, lime, chlorine, water, and a substance insoluble in acids. A quantitative analysis gave the following numbers :—

Copper	36·34
Lime	11·61
Peroxide of iron	7·87
Carbonic acid	9·32
Chlorine	0·25
Water	0·28
Residue	25·23
	90·90

The chlorine in the mineral was associated with copper, oxide of copper, and water, forming the oxychloride of the metal, and the carbonic acid with the lime, as 11·61 of that earth requires 9·12 of carbonic acid to form a carbonate, and analysis shews 9·32. The greater part of the copper evidently exists as protoxide, and the constitution of the mineral may be thus expressed:—

Oxide of copper	42·92
Oxychloride of copper ($3CuO, CuCl, 4HO$)	2·89
Carbonate of lime	20·73
Peroxide of iron	7·87
Residue	25·23
Loss	0·36
	100·00

If the impurities be removed, viz., the residue insoluble in acids, peroxide of iron and carbonate of lime, we obtain

Oxide of copper	93·69
Oxychloride of copper	6·31
	100·00

Black Amorphous Sulphate of Lead.—An exceedingly curious form of sulphate of lead was found in a mine a few leagues N.W. of Coquimbo. It occurred in large black masses, in the centre of which a small vein of finely grained galena was running. The sulphate, having a black earthy appearance, with no trace of metallic lustre was rejected by the miners as worthless. Its high specific gravity proved however that it consisted essentially of a compound of one of the heavier metals, and analysis shewed that it was sulphate of lead coloured with a small percentage of protoxide of iron. Hydrochloric acid at the boiling temperature decomposed it entirely, forming a pale green solution, due to protochloride of iron, or rather perhaps protosulphate, as free sulphuric acid existed in the liquid, and on cooling the greater part of the lead was deposited as chloride. Sp. gr. of the mineral 6·20 100 grs. yielded

Sulphate of lead . . .	96·74
Protoxide of iron . .	3·16
Silver	traces
	99·90

The galena, which formed as it were the nucleus of the mass contained (as is generally the case with the fine-grained sulphide of lead) appreciable quantities of silver, far more so than the exterior sulphate.

Basic Persulphate of Iron.—This beautiful mineral has been described in mineralogical treatises as *fibroferrite*. As however numerous sulphates appear to exist, among which may be mentioned, Fe_2O_3, SO_3, generally cited in chemical works as the one found native in South America, an account of the true fibroferrite may not perhaps be out of place.

This mineral is found in botryoidal masses, each rounded nodule being built up of innumerable silky fibres diverging from the centre, and of a pale golden green colour. It consists of two equivalents of sulphuric acid in combination with one of sesquioxide of iron (Fe_2O_3, $2SO_3$), and 10 of water.

	Calculated.	Found.
Sulphuric acid . .	32·0	31·94
Peroxide of iron . .	32·0	31·89
Water . . .	36·0	35·90
	100·0	99·73

After exposure to the air for a few weeks, it loses two equivalents of water and becomes $Fe_2O_3,2SO_3,8HO$, and does not decrease further in weight even after many months. Heated in a water bath at 212°F., it loses 7 atoms of water, the residue consisting of $Fe_2O_3,2SO_3,3HO$, and it requires a very high temperature for the expulsion of the last 3 equivalents. When subjected to a temperature of between 500° to 600° F. for some hours, the whole of the water is expelled and a pure bisulphate of peroxide of iron, perfectly anhydrous, remains.

	Calculated.	Found.
Peroxide of iron .	50·00	49·87
Sulphuric acid . .	50·00	49·98
	100·00	99·85

When fibroferrite is digested in cold water, it is partially dissolved, the solution containing both iron and sulphuric acid, and having a slightly acid reaction to test paper. The phenomena produced by the action of boiling water are interesting. The mineral becomes decomposed at a temperature of about 120° F., into an ochreish yellow amorphous substance, and a soluble salt, the solution of which is strongly acid. 10·00 grains of fibroferrite were digested in boiling water for an hour, and the residue dried on a water bath at 212. This insoluble portion weighed exactly 3·00 grains, and yielded on analysis 2·100 peroxide of iron, ·528 sulphuric acid, and ·368 water, being evidently a combination of 2 equivalents of peroxide of iron, with 1 of sulphuric acid, and 3 of water.

	Calculated.	Found.
$2\ Fe_2O_3$ . . .	70·49	70·00
$1\ SO_3$ . . .	17·61	17·60
3 HO . . .	11·90	12·26
	100·00	99·86

or $2Fe_2O_3,SO_33HO$.

The sulphuric acid in the filtrate was found to weigh 2·640, and the peroxide of iron 1·06, the loss agreeing very closely with the 7 equivalents of water which separated at 212°.

Sulphuric acid evidently exists in a free state, as well as in combination with peroxide of iron, as the persulphate. Thus it appears that 3 equivalents of fibroferrite have split up into 1 equivalent of a very basic sulphate, 1 of ordinary sesquisulphate, 2 of free sulphuric acid and water.

$$3(Fe_2O_3,2SO_3,10HO) = 2Fe_2O_3,SO_3 + 2SO_3 + Fe_2O_3,3SO_3 + xHO.$$

The insoluble compound described above is found native, and very often associated with fibroferrite. Should the sesquisulphate of iron and free sulphuric acid come in contact with sesquioxide of iron and water, fibroferrite might be reproduced.

$$2(Fe_2O_3,3SO_3, + 2SO_3) + 3Fe_2O_3 + 50HO = 5(Fe_2O_3,2SO_3, + 10HO).$$

It is somewhat singular that from Fe_2O_3, $2SO_3$, in which two atoms of acid are united with one of base, a compound with two of base with one of acid should be derived.

Bournonite.—Bournonite was unknown in South America, and I believe in the New World, until the year 1858, when I met with it in a mine near Huasco, in the northern part of Chile. The specimen was crystallized. Hardness 2·5; specific gravity 5·80. It resembled in every respect the samples found in Cornwall and some parts of Germany. 100 grains yielded—

Sulphur	20·45
Antimony	26·21
Lead	40·76
Copper	12·52
	99·94

A specimen from Cornwall gave—

Sulphur	20·30
Antimony	26·30
Lead	40·80
Copper	12·70
	100·10

This mineral is mentioned in the present memoir not only as being the first of the kind found in America, but also for the purpose of introducing a few remarks, relative to the separation of arsenic and antimony, from lead, copper, and other metals of that group. In 1854 MM. Rivot, Beudant, and Daguin, published a very interesting paper in the *Comptes Rendus,* wherein it was proposed to separate antimony, arsenic, and sulphur from many other elements, by digesting the mineral in a warm solution of potash, which after a time dissolved the arsenical and antimonial sulphides, and passing a stream of chlorine through the potash solution, by which were formed sulphuric, arsenic, and antimonic acid. By adopting this means, the authors remark, the whole of the antimony, arsenic, and sulphur, may be removed from lead, copper, &c. I have repeatedly tried this process, and although in my experiments, the minerals were in a very finely divided condition, complete decomposition, especially when antimony was present, could not be effected. In most instances, much of that element and nearly all the arsenic were dissolved, but even after many days digestion, antimony was invariably found in the residue. Hypochlorites of the alkalies or alkaline earths do not answer better. Dr. Aug. Streng (Ann. Ch. Pham., xcii, 411, and Chem. Gaz., xii, p. 269), endeavoured in his volumetrical determination of lead, to decompose galena with hypochlorite of lime, but without success. I also have tried hypochlorite of soda upon that and many other minerals with equally unsuccessful results. Streng, however, acted upon the galena with strong nitric acid, thus converting it into sulphate of lead, and then, after neutralizing the fluid with potash, digested, at a temperature a little below 212°F., with chloride of lime, when after some time, decomposition was complete, the whole of the sulphate of lead having passed into the state of peroxide. When bournonite is treated in the same way, chloride of soda being employed, instead of the lime-salt, a considerable quantity of antimony passes into solution, but 2 or 3 per cent. always remains in the residue.

The process answers admirably in the analysis of copper or lead minerals containing arsenic and sulphur. For *guayacanite*, ($3Cu_2S,AsS_5$) for example, the mineral is finely pulverized, digested in fuming nitric acid, and evaporated nearly to dryness; hypochlorite of soda is then added in considerable excess, and the whole boiled for about 20 minutes. All the arsenic and sulphur pass into the filtrate, pure oxide of copper remaining undissolved.

The same is the case with the sulpho-arsenides of cobalt and nickel. The stronger solutions of potash and soda in very great excess, and after violent ebullition, fail to decompose the arseniates of these metals completely; but if a stream of chlorine be passed through the alkaline liquid previous to boiling, or which is simpler, a hypochlorite be at one employed, no trace of arsenic can be detected in the residual oxides.

Double Sulphide of Copper and Lead.—This very rare mineral, which I discovered in a mine near the silver district of Arqueros, consists of three equivalents of disulphide of copper and one of sulphide of lead, differing entirely from *Cuproplumbite* $Cu_2S, 2PbS$, also from Chile, which was analysed by Plattner, many years ago. 100 grs. of the new double sulphide yielded—

Copper	53·28
Sulphur	17·69
Lead	28·81
	99·78

or $3Cu_2S,PbS$

	Calculated.	Found.
$3Cu_2$	53·34	53·28
4S	17·78	17·69
1Pb	28·88	28·81
	100·00	99·78

It may be mentioned that this mineral has received the name *Alisonite,* in honour of Mr. Robert E. Alison, a gentleman who from his extensive smelting operations in no less than five different points in the Republic of Chile, has effected very much in the development of the mineral riches of South America. I observe that the great American Minerologist Dana, to whom I sent a short note upon the mineral in question, has published it under the name *Alisonite* in his supplement to the last edition of his work.

This mineral adds another to the list of the tribasic sulphides which have been already discussed in the two papers I have had the honour of transmitting to the Society.

Arsenical Rosicler	$3AgS, AsS_3$
Antimonial do	$3AgS, SbS_3$
Sulphide of copper and arsenic	$3Cu_2S, AsS_3$
Guayacanite	$3Cu_2S, AsS_5$
Alisonite	$3Cu_2S, PbS$.

Mr. David Forbes, on his return from Chile, published an account of a new arsenide of copper in the Philosophical Magazine for last December, and has named it *Darwinite*. This adds another to the list of arsenides, the first of which is *Domeykite*, and the second *Algodonite*, of which I published an account in the Journal of this Society in 1857.

Domeykite	Cu_6As
Algodonite	$Cu_{12}As$
Darwinite	$Cu_{18}As$.

XIV.—*On the action of Dibromide of Ethylene on Pyridine.*

By John Davidson.

Recent researches have proved that the bromides of the diatomic radicals are capable of fixing either one or two molecules of ammonia and the monamines, the bromides of a monamonium and of a diammonium being thus produced.

This fact having been hitherto almost exclusively established by experiments with the ethylated bases of the nitrogen and of the phosphorus-series, it appeared desirable, for the sake of generalization, to extend these observations to the several other groups of monamines.

Among the numerous bases which presented themselves for an examination of this kind, the group of basic compounds isomeric with the aromatic bases could not fail to attract my attention. Pyridine, picoline, &c., discovered by Dr. Anderson, are powerful monamines, the tertiary character of which is well established by their deportment with iodide of ethyl; the advanced degree of substitution rendered these substances particularly well adapted for the intended experiments.

Pyridine, as is well known, has been obtained in the destructive distillation of coal, of certain varieties of shale, and of animal substances. The substance* which I had at my disposal was procured from coal tar. It was separated from the picoline by distillation; the specimen with which I worked boiled constantly at 118°·5 C.

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* I am indebted to Mr. Samuel Clift, of Manchester, for a considerable supply of pyridine and all the other bases formed in the destructive distillation of coal.—A.W.H.

A mixture of pyridine and dibromide of ethylene gradually darkens and ultimately becomes brown; no crystals, however, are deposited. On the other hand, the reaction proceeds with great rapidity at 100° C.; and if this temperature be continued for about three hours, an almost black and crystalline mass is formed, from which by successive treatment with cold, and crystallisations from boiling alcohol, a beautiful bromide crystallising in silky plates may be eliminated. In preparing this bromide, it is advisable to add to the mixture of the anhydrous substances, from one-fifth to one-sixth of its volume of alcohol and to digest at 100°C. in sealed tubes; in this manner, the whole liquid solidifies into a silky crystalline mass, which, being but very slightly coloured, is much more easily purified. The new bromide may also be prepared by digesting at 100°C. a mixture of pyridine and dibromide of ethylene with an equal bulk of alcohol, in a flask provided with a condensing tube. This process, however, is less expeditious, and is apt to occasion a loss of pyridine, which may be carried off with the alcohol-vapour.

The crystalline bromide, although not deliquescent, is very soluble in water; I did not succeed in getting crystals from the aqueous solution; it is exceedingly soluble in boiling, and only slightly so in cold alcohol. The boiling alcoholic solution solidifies on cooling into a pearly crystalline mass; dilute solutions on cooling, or on spontaneous evaporation, yield larger plates, which are transparent, but were never sufficiently well formed for determination.

I. When burned with chromate of lead, 0·206 grm. of the bromide previously well dried at 100°C., gave 0·316 grm. of carbonic acid and 0·077 grm. of water.

II. 0·4165 grm. of the bromide, when precipitated by nitrate of silver, gave 0·452 grm. of bromide of silver.

The simplest expression representing these numbers is

$$C_6H_7NBr^*;$$

but the mode of formation of the new compound shows unmistakeably that this expression must be doubled, and that the compo-

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[*] $H = 1$; $O = 16$; $C = 12$ &c.

sition and weight of the molecule of this compound is represented by the formula,

$$C_{12}H_{14}N_2Br_2$$

		Theory.		Experiment.	
				I.	II.
C_{12}	=	144	41·62	41·69	,,
H_{14}	=	14	4·04	4·15	,,
N_2	=	28	8·10	,,	,,
Br_2	=	160	46·24	,,	46·16
		346	100·00		

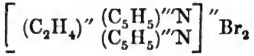
Pyridine, therefore, imitates triethylamine and triethylphosphine in its deportment with dibromide of ethylene, the new bromide being formed by the union of one molecule of the latter with two molecules of pyridine:

$$C_2H_4Br_2 + 2C_5H_5N = C_{12}H_{14}N_2Br_2$$

The constitution of pyridine itself is but imperfectly made out. All that we know is that this substance is a tertiary monamine; the nature of the radicles which replace the hydrogen is as yet unknown. In accordance with our present knowledge, pyridine is represented by the expression

$$(C_5H_5)'''N;$$

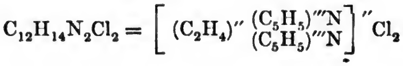
whence the molecular construction of the new bromide may be expressed by the formula



$$\left[(C_2H_4)'' \begin{matrix}(C_5H_5)''N\\(C_5H_5)''N\end{matrix}\right]'' Br_2$$

The composition of the dibromide is confirmed by the analysis of the chloride and of platinum-salt.

Dichloride.—Treatment of the dibromide with chloride of silver, yields, on evaporation of the liquid obtained, the corresponding dichloride, which is a white crystalline exceedingly soluble and deliquescent substance. 0·232 grm. of the dichloride, dried at 100°C. and cooled *in vacuo,* gave 0·259 grm. of chloride of silver, showing 27·62 per cent. of chlorine, which is exactly the percentage required by the formula



$$C_{12}H_{14}N_2Cl_2 = \left[(C_2H_4)'' \begin{matrix}(C_5H_5)'''N\\(C_5H_5)'''N\end{matrix}\right]'' Cl_2$$

Platinum-salt.—The solution of the dichloride yields, with dichloride of platinum, a pale yellow and apparently amorphous precipitate, insoluble in water or alcohol, but slightly soluble in boiling concentrated hydrochloric acid, from which on cooling it is almost entirely deposited again in the form of little brilliant yellow plates.

I. On burning the platinum-salt with chromate of lead, the following results were obtained:

0·415 grm. of substance gave 0·36 of carbonic acid and 0·1006 of water.

II. 0·312 grm. of the platinum-salt on ignition gave 0·1032 grms. of metallic platinum.

The formula

$$C_{12}H_{14}N_2Pt_2Cl_6 = \left[(C_2H_4)'' \begin{matrix} (C_5H_5)'''N \\ (C_5H_5)'''N \end{matrix} \right] Cl_2,2PtCl_2$$

requires the following values:

		Theory.		Experiment. I.	Experiment. II.
C_{12}	=	144	24·120	23·63	„
H_{14}	=	14	2·345	2·67	„
N_2	=	28	4·690	„	„
Pt_2	=	198	33·167	„	33·3
Cl_6	=	213	55·678	„	„
		597	100·00		

The solution of the dibromide, when mixed with freshly precipitated oxide of silver in the cold, furnishes a transparent, colourless, and powerfully alkaline liquid, which contains the corresponding base, viz: the *hydrate of ethylene-dipyridyl-diammonium.*

$$C_{12}H_{16}N_2O_2 = \left.\begin{matrix} [(C_2H_4)''(C_5H_5)_2''N_2]'' \\ H_2 \end{matrix}\right\} O_2$$

The existence of this compound in the solution is readily proved by saturating the caustic liquid with hydrochloric acid, and adding dichloride of platinum, whereupon the pale yellow salt previously mentioned is immediately precipitated. It was identified by analysis.

0·185 grm. of platinum-salt left, on burning, 0·0612 grm. of metallic platinum corresponding to 33·08 per cent., the theory requiring 33·16 per cent.

The hydrates of the diatomic pyridyl-derivatives are however far less stable than the ethylated diatomic bases in the nitrogen- and phosphorus-series. Even at the common temperature, and more rapidly so on heating the solution of the free base becomes pink, violet, and ultimately ruby-red, and deposits after some time a brown powder, a peculiar odour resembling that of heliotrope being evolved at the same time. I have not examined more minutely the changes which the pyridine-compound thus undergoes. I will only mention that the solution, when it had become coloured, no longer yielded the difficultly soluble precipitate with dichloride of platinum, a crystalline platinum-salt being deposited only after a considerable time; on the other hand, when boiled for some minutes, and separated from the brown compound which is deposited, the liquid again gave a yellow amorphous platinum-salt.

I have made also a few experiments with picoline, homologous to pyridine and isomeric with phenylamine. This base is likewise acted upon by dibromide of ethylene, but far less energetically than pyridine: digestion for four hours at 100°C. produced but a slight change; after digestion for several hours at about 150°C. the mixture was black, but had not deposited any crystalline matter; after several days, crystals began slowly to form. I have not examined this reaction any further.

The above experiments were performed in Dr. Hofmann's laboratory.

XV.—*Account of recent researches on the application of Electricity, from different sources, to the explosion of Gunpowder.*

By F. A. Abel, F.R.S., Director of the Chemical Establishment of the War Department.

The employment of electricity as an agent for affecting the ignition of gunpowder, suggested itself to Franklin,[*] in 1751, and to Priestley, in 1767 but it was not until some years after the discovery of the electric pile by Volta, that earnest endeavours were made to apply electricity to military and mining purposes. In 1832, the first experiments on the application of voltaic electricity in this direction appears to have been made by French Military Engineers; about twelve years afterwards, that agent was first successfully employed in important blasting operations (such as, in England, the destruction of the Round Down Cliff, near Dover, and of the wreck of the Royal George, at Spithead), and from that period until very recently, the applications of electricity to mining purposes have been almost entirely confined to the employment of the voltaic current.

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[*] In his "Letters on Electricity," dated 29th June, 1751, Franklin says, "I have not heard that anybody in Europe has yet succeeded in firing gunpowder by means of electricity. We do it in this way: a small cartridge is filled with dry powder, which is rammed in tightly enough to crush a few grains; two pointed brass wires are then fixed in it, one at each end so that their points are not further apart than half an inch at the centre of the cartridge, which is then placed in the circuit of the electric machine; when the communication is completed, the flame, leaping from the points of one wire to that of the other, through the powder in the cartridge, fires it instantaneously."

The methods which have been most generally used, up to the present time, for the explosion of gunpowder by the direct agency of voltaic batteries of different kinds, are so well known to all who have given their attention to experimental electricity, that a brief statement of the principles upon which they are based, will suffice. The original method, and that still principally used in military operations, when the voltaic battery alone is employed, consists in causing the current (at the place where the powder is to be exploded), to traverse a short piece of fine wire, made of some metal of inferior conducting power, such as platinum or iron, which, in consequence of the resistance offered by it to the passage of the current, is raised to a red heat on completion of the metallic circuit, of which it forms a portion. The thin wire is surrounded with fine-grain gunpowder, and is generally fitted into some simple arrangement, which may readily be connected with the circuit-wires, and brought into close contact with the charge to be exploded.

The other approved method of affecting the ignition of a charge of powder by a voltaic current, consists in the employment of an ingenious contrivance, first introduced by Messrs. Statham and Brunton, and founded upon an observation made in experiments with a submarine telegraph-wire, which had been insulated with gutta-percha impregnated with sulphur. Some amount of chemical action is exerted between the sulphur and the copper, in covered wire of this description, in consequence of which, the surface of gutta-percha in contact with the wire becomes coated with particles of subsulphide of copper, which remain attached to it on the removal of the wire. This coating of subsulphide is a sufficiently good conductor of electricity to assist the passage of a current of low tension across a small interruption in the metallic circuit; the heat resulting from the retardation of the current at such a point is, however, sufficiently intense to effect the ignition of some very combustible substance. It is obvious that this fact admits of ready application to the construction of an arrangement for the ignition of gunpowder, in which contrivance a hollow piece of gutta-percha, coated on the interior with the sub-sulphide of copper, is made to replace the fine platinum- or iron-wire above referred to. The Statham fuze, constructed upon this principle, has been found under favourable conditions, which have been fully discussed in other memoirs relating to this subject, to present important advantages over the method of igniting gunpowder by means of fine wires.

Although the employment of voltaic currents for the ignition of charges of gunpowder obviously presents great advantages over the old system of firing mines or cannon (by means of slow and regular-burning matches or fuzes, the length and time of burning of which was proportioned to the interval which it was desired should elapse between their first ignition and the explosion of the charge), its application, especially to military purposes, is attended with an amount of uncertainty which has precluded it from ever acquiring great confidence on the part of engineering authorities. This uncertainty is, it need scarcely be said, due mainly to the great difficulty of ensuring a sufficient uniformity of action at different periods of time, even with the most efficient voltaic arrangements, and of securing the safe transport and proper preservation of any battery-arrangement, and of the agents necessary for its application. When it is remembered that, besides these difficulties, there are others not less serious, which result from the uncertainty of ensuring proper attention to the numerous little points, of vital importance to success, connected with such an application of electricity of low tension, it will be readily conceived that, almost ever since the first practical application of electricity to the ignition of charges of powder, the possibility of rendering electricity of high tension available in this direction, and of applying to military operations the valuable discoveries of Faraday in electro-magnetism, has received from time to time, serious attention on the part of military engineers and others specially interested in operations of this kind.

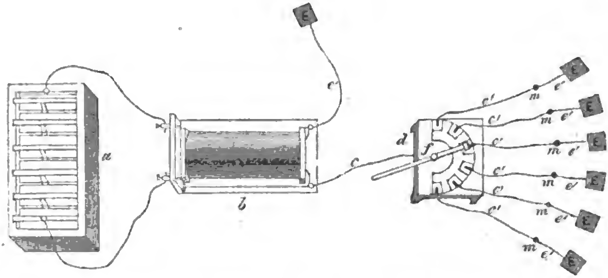
Thus, experiments furnishing interesting and important results have been instituted on the application of induced currents, and of frictional electricity to the explosion of gunpowder, in Spain, France, Austria, Russia, and other countries; and, in 1855, Professor Wheatstone suggested to General Sir John Burgoyne the institution of an experimental enquiry in this country into the relative advantages offered by electricity of high tension, obtained from different sources, as applied to the explosion of gunpowder. In consequence of this suggestion, a long series of experiments has been carried out by Professor Wheatstone and myself, by desire of the Secretary of State for War, and, at first, in connection with the Ordnance Select Committee. The most interesting and important of the results arrived at by those investigations will form the principal subjects of this memoir.

Although our experiments with volta-induction apparatus, with frictional electricity, and with the currents induced by permanent magnets, were conducted, in great measure, at the same time, it will be advisable to avoid confusion by giving, under separate heads, on account of the results furnished with each form of electricity, and of the conclusions deduced from them.

I.—EXPERIMENTS WITH ELECTRO-MAGNETIC INDUCTION APPARATUS.

The first application, with practical success, of the form of electricity furnished by volta-induction apparatus to military purposes was made in 1853 by a Spanish officer, Colonel Verdu, who, having witnessed the firing of a gun at Dover by the agency of a voltaic battery at Calais, connected with the gun by means of a submarine cable, was much struck with the inconvenience resulting from the necessity of employing very great battery-power for effecting the discharge of gunpowder at considerable distance, it having been necessary on this occasion to use a battery of 400 of Bunsen's cells. The first investigations of Colonel Verdu were made with the assistance of M. Ruhmkorff, and with the induction coil-machine which had been recently perfected by the latter. The success attending the first experiments led to further trials in Spain, where Colonel Verdu succeeded, with the employment of only one element of Bunsen's battery, in exploding simultaneously six mines in one circuit, at a distance of 300 metres. This result was, of course, obtained by allowing the current to leap across small interruptions in the metallic circuits, which were surrounded with a readily inflammable substance, and imbedded in the charges of powder. The fuze employed was, in fact, that of Statham, in which the terminals were surrounded by fulminate of mercury. Still greater results were obtained by arranging the mines in groups of five, so that each group formed a special circuit; by then bringing each circuit, in very quick succession, in connection with the instrument, the mines were all discharged with a rapidity which had the practical effect of a simultaneous discharge. The reason why Colonel Verdu resorted to this method of operation is, that the discharge from an induction coil-machine, unlike that from a Leyden jar, which will pass through several hundred solutions of continuity, producing a spark at each interruption, becomes so enfeebled by successive interruptions in the metallic circuit, that it is impracticable to ignite, with certainty, a number of charges in one circuit, beyond certain limits, which, with the fuzes used by Colonel Verdu, were very narrow.

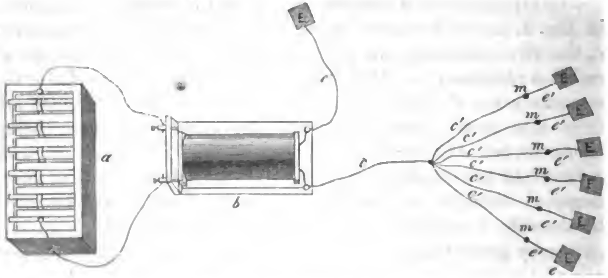
Fig. 1.



The arrangement of charges, &c., upon this system is exhibited in Fig. 1, in which *a* and *b* represent the battery and coil-machine; *c*, the wire connecting one pole of the latter with an instrument, *d*, called a *rheotome*, provided with binding screws for receiving the separate wires *c′*, which lead to the mines *m*. These screws are fixed into small copper plates isolated from each other, being either let into the wood, or separated by strips of glass. The wire *c* from the coil-machine is in connection with a species of metal finger, *f*, which, by means of an insulating handle, may be made to describe a semicircle with optional rapidity; and, as its one extremity presses firmly upon the instrument at a point near any one of the binding screws, it is brought alternately into contact with the several small metal plates with which they are connected, thus bringing them (and therefore the mines) into connection with the coil-machine. This is only one of several contrivances which have been used for producing successive discharges of mines upon this principle. In the above arrangement, the wires *e′* and the plates of metal E connect the charges and coil-machine with the earth.

A method of securing the practically simultaneous discharge of a number of mines, more effective than the so-called *rheotomic* arrangement of Colonel Verdu, was afterwards devised by M. Savare, who appears to have first conceived the idea of dividing the circuit into branches, over the whole of which a current, or rapid succession of currents, are distributed, on the completion of the circuit, with an uniformity regulated by the degree of resistance met with in each branch. Thus, on interposing one or more fuzes in each branch of the circuit, those which happen to offer greater facilities, in their construction, to the passage of the current, would explode first, and, the fuzes being so constructed that the terminals of the wires in them are forced apart by the explosion or fused by the heat generated, the further passage of the current in that direction is prevented, and the remaining fuzes are in their turn exploded. It is readily conceivable that, with the employment of currents of high tension, following each other with the enormous rapidity with which they pass off from the coil-machines, the discharge of a number of fuzes may be effected by the above arrangement with a rapidity which has practically the effect of a simultaneous discharge. Experiments with this mode of discharge were made at Grenelle in 1854. The arrangement of charges, discharging instrument, connections, &c., is illustrated by Fig. 2, which scarcely needs special explanation (the

Fig. 2.



letters of reference used corresponding in their meaning to those in Fig. 1, and the principal difference being that the branch-wires are connected directly with the wire leading to the machine, instead of by the agency of a rheotome.)

The Ruhmkorff's coil appears, without doubt, to have been used by the Russians in their mining operations at Sebastopol. But the most extensive application hitherto made of that instrument for the explosion of mines has been in the great operations undertaken by Messrs. Dussaut and Rabattu at the Port of Cherbourg, in 1854, according to a system organized by the Vicomte du Moncel, and which was a modification of Colonel Verdu's method. At the first trial, six mines, containing each about 4,400 kilos. of powder, were inflamed as with one detonation, detaching at once more than 50,000 cubic metres of rock.

When the experiments at Woolwich were first undertaken in 1856, much uncertainty appeared still to prevail regarding the description of priming materials best adapted for employment in fuzes to be used with the volta-induction current, and the maximum number of charges which could be fired *with certainty* by means of a powerful coil-machine and a battery of moderate power. Experiments were therefore undertaken to obtain information on these points, and to ascertain the extent to which an electro-magnetic coil, of the best and most portable construction, would be likely to resist injury by ordinarily careful use and by transport.

The coil-machine used in the first experiments was one of considerable size and recent construction, prepared by M. Ruhmkorff. Another apparatus, of similar power, but constructed for the Ordnance Select Committee by M. Ruhmkorff, with especial regard to its service in the field, was also subsequently employed in many of the experiments. A battery of cast-iron cells and zinc plates (the dimensions of the latter being 5 in. by 3 in.) was employed, as the most economical for general purposes.

In the greater number of the experiments, the current was made to pass to the charges or fuzes through one mile of copper wire (16 gauge), insulated with gutta-percha, the metallic circuit being, in many instances, interrupted by an earth-connection of about 200 yards in length.

The results furnished by a large number of experiments were briefly as follows:—

Fine-grain or mealed gunpowder was found to be ignited readily, by means of the induction-coil, with the employment of one cell of the battery. Numerous substances of a more highly explosive character were tried, alone, and in admixture with gunpowder, in order to arrive at the description of priming material most suitable to aid in effecting the ignition of the maximum number of charges by means of the coil-machine. The best results were obtained with fulminate of mercury. The efficacy and delicacy of the fuze were also found to depend in very great measure upon a proper adjustment of the wire-terminals which it enclosed.

The number of charges placed in succession, in single circuit, which could be fired at one time by means of such coil-machines as those used, and with the employment of twelve cells of the battery specified above, did not exceed eight (and was generally below that number) even when priming compositions of a sensitive character, containing fulminate of mercury, gun-cotton, sulphide of antimony and chlorate of potassa, &c., were employed. The discharge of this number could not, however, be relied upon with any certainty; and the employment of twelve cells did not appear to offer any decided advantage over the use of only four. The ignition of two charges could be effected almost with certainty by the employment of only one cell, and the result appeared to be rendered certain by the use of four cells.

By employing a rheotomic arrangement for changing the direction of the current, so as to bring wires connected with one or more charges successively into the circuit (as described just now), a considerable number of charges could be fired in very rapid succession. This result was, however, perfectly certain only when a single charge was brought into the circuit at one time.

Upon employing M. Savare's arrangement of branch-circuits, so as to allow the current, when established, to distribute itself along each divided portion of the circuit, and ignite simultaneously, or in rapid succession, the several fuzes which were introduced, five or six charges were exploded at one time, and a far more considerable number ignited, with a rapidity almost instantaneous; as, when this arrangement is employed, the first of the very rapid succession of currents established by the coil-machine passes through and ignites those fuzes which offer the least resistance, while the others are fired in their turn by the succeeding currents. This method of exploding a number of charges at once, or in very rapid succession, is undoubtedly more efficient than the best rheotomic arrangement, and it renders the operator independent of the uncertainty of firing three or four charges simultaneously, when arranged in a simple circuit; for, in the latter case, if the ignition of the whole number is not perfectly instantaneous, the explosion of the first prevents the discharge of the remainder; while, in the arrangement just referred to, the connection of each fuze with the instrument is independent.

In the course of these experiments carried on with the two coil-machines constructed by M. Ruhmkorff (one of which was, as already stated, specially prepared for operations in the field), a considerable irregularity was observed in the power of the same machine at different periods, although the battery-power employed was, to all appearances, the same on each occasion,—an irregularity which must be ascribed to defective insulation, arising from the deposition of moisture on some portion of the apparatus. It was found that the arrangement attached to the coil-machine, known as the condenser, and upon which the intensity of the current produced greatly depends, was very liable to be put out of order in the transport of the apparatus, and by other trifling causes; any derangement of this part of the apparatus was fatal to its efficiency. The perfect insulation of each coil of the secondary wire and other somewhat delicate portions of the apparatus, were also found liable to injury from a variety of sources, which it would be very difficult to guard against in the employment of coil-machines for field purposes, and by persons not thoroughly acquainted with their somewhat complicated construction and their action.

Although, therefore, the system of exploding charges by means of the induction coil-machines, offers several very important advantages over the voltaic battery, employed alone (one of the principal being the great reduction effected by its use in the power of battery required) its adoption as a general substitute for the old system of operation with the battery cannot be recommended with confidence, principally because proper reliance cannot be placed upon the certainty and permanent uniformity of action of the apparatus.

Some experiments which I have instituted quite recently, combining the use of one of the coil-machines above referred to, with that of the new description of fuze devised by me for employment with magneto-electric apparatus (to be presently described), furnished results greatly surpassing in magnitude and certainty any which have hitherto been obtained with volta-induction currents.

Employing only six cells of a small Smee's battery, from ten to fifteen charges were fired with certainty when arranged in a simple circuit; fifty charges (arranged in branch circuits, in sets of ten) were ignited with the effect of one explosion, and there is no doubt that this result might be considerably exceeded with the introduction of a larger number of branches into the circuit arrangement.

It must be borne in mind that these results were obtained with a coil-machine made by Ruhmkorff in 1855. The very important improvements which have recently been effected by Ladd, Bentley, Ruhmkorff, and others in the construction of the induction coil-apparatus, have reduced to comparative insignificance the most powerful results furnished by the Ruhmkorff coil, as constructed five or six years ago. There is no doubt that, with the combined employment of the new fuzes and of one of the larger induction coil-machines of recent construction, the simultaneous ignition of several hundred charges could be effected without difficulty, and that, in operations of very great magnitude, such an instrument may be employed with confidence as the most efficient agent for effecting the explosion of mines.

II.—EXPERIMENTS WITH FRICTIONAL ELECTRICITY.

It has already been stated that, as early as the middle of the eighteenth century, Franklin and Priestly both directed their attention to the application of electricity from the machine to the ignition of gunpowder; but it was not until 1831 that an actual application of frictional electricity to mining purposes was first made by Moses Shaw, of New York, who, with fuzes charged with gunpowder and fulminate of silver, succeeded in exploding several mines simultaneously, detaching large masses of rock. It is stated by him, in his account of the experiments, that he was unable to operate during the greater part of the year, on account of bad weather. In 1842 and 1843, Messrs. Warrentrap, of Brunswick, and Götzmann, of Freiburg, made more successful experiments. Having effected improvements in the insulation of the conducting wires used, and employing fuzes which contained a mixture of sulphide of antimony and chlorate of potassa, they succeeded in exploding from eight to ten mines simultaneously through 78·5 metres. Notwithstanding these results, they were compelled to abandon the attempt to employ electricity as a certain agent for the explosion of gunpowder, on account of the evil influence of atmospheric moisture. In 1845, the subject was again brought up by Mr. Charles Winter, who succeeded in inflaming powder through a telegraph wire, reaching between Vienna and Hetzendorf, a distance of 4,906 metres.

In 1853, when the first successful results had been obtained in France with the Ruhmkorff coil, the Austrian Government directed the Imperial Engineer Academy to propose a system of exploding charges by electricity, to be employed by the Imperial Engineers.

The somewhat complicated character of the induction coil-machine, and the necessity for the employment of some voltaic battery with it, appear to have been accepted, at the outset, by the Austrian investigators as formidable obstacles to the application of the apparatus in question to military purposes. Attention was therefore again directed to the application of frictional electricity; and, after three years' experiments, a system of operation, involving the employment of an electric machine, was considered to have been sufficiently successful for introduction into the engineer service. The system in question appears to have furnished very important results, and to have been frequently applied to industrial operations.

The electric machine employed is arranged in a very portable form, and consists of two discs of polished glass, twelve inches in diameter and four lines thick, fixed upon one axis, within 1½ inches of each other, and fitted with cushions to which springs are attached. The Leyden jar is cylindrical, fifteen inches high and six in diameter (its area being 276 square inches). It is protected by flannel and fixed in a case of lacquered tin, being screwed on to an iron plate which is connected with the friction-apparatus. The charging is effected by means of a steel point, which projects one inch into the space between the discs, and can be pushed into an arm of the conductor. The latter is inserted into a plate of hard caoutchouc which forms the cover of the Leyden jar, and is connected by chains with its inner surface. The machine is always covered, when in use, by a case, the sides of which are made of thick leather and the top of tin. A small stove is also fixed beneath it, so as to dry the air inside when necessary. The wire employed as conductor is brass, which is raised on insulated posts or covered with gutta-percha; the priming material used in the fuzes was, first fulminate of mercury; a mixture of chlorate of potassa and sulphide of antimony was afterwards adopted. A large number of experiments were tried with this arrangement, under the various conditions in which it might receive application. The greatest distance at which an inflammation was attempted was four German miles. On several occasions, fifty mines were simultaneously discharged in the same circuit; the fuzes were two klafters (toises) from each other, and the electric machine was 140 klafters from the nearest fuze. In like manner, thirty-six charges were simultaneously exploded in one of the branches of the Danube; these charges were placed six feet under water, and had remained submerged during twenty hours previous to their explosion. Other operations on a large scale, in marble quarries, in the beds of rivers, &c., in which considerable masses of matter were displaced, are given in detail in an interesting report by Baron von Ebner, published in 1855; they place the efficiency of the process beyond doubt. The objections to the system, as pointed out in the report referred to, are that some scientific skill is required in the manipulations; that great care is needed in the preservation of the apparatus, and that the inductive action is sometimes so energetic that explosions are occasionally determined in other mines not intended to be included in the series, and not connected with the machine.

At the suggestion of Mr. Wheatstone, a series of experiments was undertaken for the purpose of ascertaining whether the hydro-electric machine of Sir William Armstrong might not be advantageously substituted for the ordinary electric machine for charging a Leyden jar or battery in the field.

A small portable hydro-electric machine was constructed specially for the enquiry, and placed at the disposal of the experimenters by Sir William Armstrong. It consisted of a small vertical boiler (supported on a sheet iron stand in which a grate was fixed), of two gallons capacity, provided with a safety-valve, by which the pressure of steam could be regulated up to 90lbs. on the inch. The head of the boiler was provided with a cock, to admit of the escape of steam, to which was fixed a horizontal iron pipe, nine inches in length, and of half an inch internal diameter, and fitted with the jet and wooden cylinder which serve for the issue of the steam and the development of the electricity. The iron pipe was surrounded by a small metal box, which, when the apparatus was in use, was partly filled with water, so as to effect a partial condensation of the vapour as it passed through the pipe.

A brass fork, raised to a level with the jet, and capable of adjustment at different distances from it, served the purpose of conducting the electricity from the jet of steam to the Leyden jar or jars, which were placed in a sheet-iron casing, immediately under the steam-jet. The boiler was very well adapted to the rapid generation of steam of considerable pressure. About twenty minutes after a wood fire was kindled, a pressure of 60–70lbs. was obtained, the boiler being one-third full of water.

To avoid the possibility of the water in the boiler *priming* during an operation, in which case the charge of a jar with electricity could not be accomplished, it was indispensable that the boiler should not contain too large a quantity of water (it was found safest to employ it not more than one-half full), and that the water should be free from solid matter in suspension. To ensure the fulfilment of the latter conditions, it was necessary, not only to employ perfectly clear water, but to clean out the boiler after each experiment (if spring or river-water were employed), so as to remove all solid matter deposited by the boiling water. With the employment of rain- or distilled water, this precaution was, of course, rendered unnecessary. The time required to charge with electricity a Leyden jar of about 1⅓ square feet surface, when the machine was in good working order, was found to be from five to seven seconds. The rapidity with which the jar was charged proved, under favourable conditions, to be proportionate to the pressure of steam employed, the most suitable being from 60–70lbs. per square inch.

The first experiments on the ignition of charges were conducted with the employment of only short lengths (from 12 to 50 feet) of wire, to serve as connections between the jar and the charges. The machine was worked in a locality sheltered from wind and draught. The priming composition employed in the charges was the same as that ultimately adopted in the experiments with the magnet, which will be presently described. Two different plans were available for firing the charges: (1.) by completing the circuit before the jar was charged, and allowing the fuzes to be fired by its spontaneous discharge; (2.) by allowing a definite time (about six or seven seconds) for the charging of the jar, before completing the circuit. The first method would be preferable for the ignition of a very large number of charges in the same circuit, as the employment of the maximum charge attainable would thus be secured. If, however, the ignition of the charges had to be effected at a given time, it would be necessary to employ the second method.

The results obtained by this apparatus were very variable. On one or two occasions (five seconds being allowed for the charging of the jar), it was found impossible to fire six charges, placed in a simple circuit, simultaneously, with certainty; although, when eight, and afterwards twelve, were connected in a similar manner, seven and eleven were fired, the conditions (as to pressure, &c.) being apparently the same. On another occasion, with a pressure of 70 lbs., and an allowance of seven seconds for the charging of the jar, forty fuzes were placed in circuit, and the whole number discharged. One hundred and twenty were afterwards placed in circuit, and of these, one hundred were instantaneously discharged. Attempts were subsequently made, under apparently the same conditions, to obtain a repetition of these results, but without success. Experiments made to effect the ignition of several charges in circuit, through a considerable length (one mile) of covered wire and an earth-connection, were only very partially successful. At first the greater portion of the wire was left in a coil, for the sake of convenience, and only a short earth-connection (about twenty feet) was employed. Very successful, though not uniform, results were obtained, forty and fifty fuzes (the entire number in circuit) having, in some instances, been ignited, while, in others, a few were left in different parts of the circuit.

Upon uncoiling the wire to the extent of about 600 yards, and causing the circuit to be completed by the earth, these results could not be in any way depended upon, and on no occasion were as many as forty charges fired, the number at times not exceeding five or six.

A few experiments made with small Leyden jars, charged with electricity from the ordinary cylindrical machine, were confirmatory of the comparative uncertainty in firing a large number of charges through an extended metallic circuit of considerable length. Forty charges were fired by means of a Leyden jar, containing sixty square inches of surface, the electricity passing through about twenty feet of wire-circuit; but on employing one mile of wire, with an earth-connection, the ignition of twenty-five charges, though once or twice successful, could not be depended upon.

Attempts were made on two occasions to employ the hydro-electric machine in the field. At Chatham, the machine was placed in the open air, on rising ground, and 880 yards of covered wire were employed, of which about sixty were extended, an earth-connection of that length being used in place of a second wire. Two Leyden jars, each affording about 1¼ square feet of surface, formed the battery. They were enclosed in a stout wooden box, and every precaution was taken to have them dry at the commencement of the experiments. The time to be allowed for the charging of these jars, as determined by previous experiments, made in a sheltered locality, was about ten seconds, with the employment of steam at 70 lbs. pressure. The atmosphere was dry, and a slight breeze blowing on the day of experiment. The machine was so placed that the steam-jet should be as little as possible affected by the wind.

Repeated unsuccessful attempts were made to fire fifty charges in circuit; these were then gradually reduced to twenty, when only five were ignited in different parts of the circuit. It was found impossible to charge the jars to more than a very slight extent. This unfavourable result was ascribed, partly to an interference of the slight wind with the steadiness of the jet of steam, and partly to the difficulty of maintaining the Leyden jars in a suitably dry condition. The machine was removed to a trench of some depth, for the purpose of sheltering the steam-jet from the wind, but with no better result. On a second occasion, the machine was sheltered from the wind, which blew freshly, by being placed under a shed. Forty fuzes were placed in circuit, with 200 yards of covered wire, coiled up, and an earth-connection of about twenty feet. The two Leyden jars were employed, and the whole of the charges were simultaneously ignited. The wire was afterwards uncoiled, and the same number of fuzes were again placed in circuit, but these did not fire. On reducing the number to twenty-five, nineteen were exploded, six being left in different parts of the circuit.

These experiments appear to prove beyond doubt that the details, or rather the auxiliaries, of the hydro-electric apparatus employed, must undergo some considerable modifications before anything like definite results can be obtained with it. Arrangements for securing the preservation of the jars in a sufficiently dry condition, and for screening the jet of steam from the prejudicial influences of the wind or draught, might readily be carried into effect, and would unquestionably contribute greatly towards rendering the apparatus more certain in its action.

The results above noticed were, however, sufficiently definite to indicate that, in mining operations of a very extensive character the destruction of docks, bridges, &c.), where it is desirable to ignite a very large number of charges simultaneously, and at which, as is most generally the case, full appliances and conveniences are at command for thoroughly fulfilling every condition of success, the hydro-electric machine is susceptible of very effective application, though scarcely with the same degree of confidence as could be placed in the certainty of action of volta-induction apparatus of recent construction. For general use in the field, the hydro-electric machine, even if its appliances are arranged in a much more efficient manner than was the case with the one employed, could certainly not be relied upon with the necessary confidence, principally on account of the difficulty of ensuring, in the field, the fulfilment of those conditions which appear essential to the proper generation of electricity by means of the steam-jet.

III.—EXPERIMENTS ON THE APPLICATION OF PERMANENT MAGNETS TO THE EXPLOSION OF CHARGES AND TO SUBMARINE OPERATIONS.

The ignition of gunpowder by the direct magneto-electric current, though well known to be practicable, has never yet been applied to military or industrial operations, and no satisfactory experiments appear to have been made, before those undertaken at Woolwich, showing its practical applicability to these purposes.

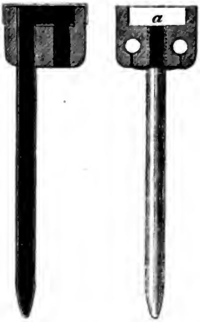
In the first experiments on this application of the magneto-electric current, a very large powerful magneto-electric machine was employed, which had been constructed by Mr. Henley (and had been exhibited by him at the Paris Exhibition in 1855). The principle of this instrument was precisely the same as that of the machine devised by Mr. Wheatstone, for ringing magneto-electric bells. Its armature, instead of being rotated, was suddenly detached from the magnet by means of a lever. It was soon established by a few experiments that, even with this instrument, gunpowder itself could not be ignited with any degree of certainty. Results obtained with Statham's and other fuzes, though superior to those furnished by gunpowder alone, were still far from satisfactory. The first efforts were therefore directed to the discovery of a suitable agent to serve as a perfectly certain medium (or priming material) for effecting the ignition of charges by means of the magneto-electric machine. For this purpose, a variety of compounds and mixtures of a more or less sensitive character, were prepared for trial with the magnet. The following were the principal tried: mixtures of meal powder with powdered coke, with sulphur, with sulphur and iron filings, with iron filings and carbon, with fulminate of mercury, and with the latter in addition to iron filings and to coke; fulminate of mercury percussion-cap composition, alone, and with coke; detonating composition (sulphide of antimony and chlorate of potassa); the same mixed with iron filings and with coke; gun-cotton alone, and mixed with some of the above; amorphous phosphorus, in admixture with oxidising agents. It will be observed that the nature of the above materials was varied so as to test the sensitiveness of readily ignitable substances, both alone, and when mixed with bodies which would serve as electrical conductors.

Many of these compositions furnished results to a certain extent favourable, a number of fuzes, primed with them, having been fired in succession with the magnet, and from two to four charges in one circuit having been ignited, in a very few instances. But no perfect certainty of discharge was attained with any one of the above materials; the attempt to fire a fuze being frequently unsuccessful, while no difference between it and a successful fuze, containing the same composition, could be detected by careful examination. These preliminary trials, however, established the fact that the sensitiveness (ready explosiveness) of a priming material was not alone sufficient to determine its success, but that those which possessed a certain, though not too considerable degree, of conducting power, were more readily and certainly ignited than others of a far more sensitive character.

Some successful results, obtained accidentally with one of the experimental compositions, which had become damp by exposure to air, led to a trial of the effect of moisture in promoting the ignition of but slightly sensitive compositions, and it was ultimately found that the impregnation of ordinary gunpowder with a small amount of moisture (by an expedient similar in principle to one adopted with considerable success by Captain Scott, R.E., in connection with charges to be fired by the induction coil-machine), rendered its ignition by means of the magnet a matter of certainty.

Some important precautions were, however, indispensable to the attainment of this definite result. If the slightly damp powder was employed in a finely divided condition, it very frequently became caked between the wire-terminals in the fuze, and the current would then pass through the composition without igniting it. This was found to take place occasionally, even when the powder was employed in its original granular condition. Several attempts were made to overcome this difficulty by modifying the form and position of the terminals or poles in the fuze, and I at last contrived a perfectly successful arrangement in which only the *sectional surfaces* of the terminals, consisting of fine copper wire (0.022 inch diameter) were exposed in the interior of the fuze (see ***a***, fig. 3), so as not to project at all. The prepared gunpowder, therefore, simply *rested* upon the surfaces, and a perfect uniformity in the action of the fuze was attained. The priming composition consisted of fine-grain gunpowder, which had been soaked in an alcoholic solution of chloride of calcium, of a strength sufficient to impregnate the grains with from one to two per cent. of that salt. The prepared powder was exposed to the air for a short time, to permit of a sufficient absorption of moisture by the deliquescent salt. Upwards of 500 quill-fuzes (of the description employed for firing guns), primed with the prepared gunpowder, and fitted with the arrangement of the terminals above referred to (fig. 3), were fired with the larger lever-magnet. The failures did not amount to more than 3 per cent., and were all proved to be due to defective manufacture. In the experiments with these fuzes, one or two simple rheotomic arrangements, such as that referred to in the first part of this memoir, were successfully employed for effecting the rapidly successive discharge of a series of fuzes.

Fig. 3.



The above fuze was found to be easy of manufacture and permanently effective. While, however, it presented a certain means of effecting the ignition by the aid of a powerful magnet, of single charges, or of a large number, to be fired in moderately rapid succession, it was inapplicable to the ignition with certainty of more than one charge in circuit. After a great number of experiments, I at length succeeded in the production of a priming material for the fuze, which greatly exceeded in sensitiveness any of the other compositions hitherto tried. A very gradual separation of the armature from the large magnet sufficed to effect the ignition of the fuzes primed with this material, and the induced current obtained by means of a very small magnet, with a rotatory armature, such as employed in Wheatstone's magneto-electric telegraph, was sufficiently powerful to produce the same result. I have recently found that the currents obtained from magnetic instruments of inferior power and less perfect construction, such as the small American magneto-electric medical apparatus, readily ignite this priming material, and that fuzes primed with it are fired with certainty, by the smallest electro-magnetic apparatus, with the employment of one moderate-sized cell of Smee's battery.

The new priming composition consisted of a very intimate mixture of sub-phosphide of copper, chlorate of potassa, and levigated coke, the latter substance being employed to add to the conducting power of the mixture, which was found otherwise insufficient.

In the course of experiments subsequently carried on with fuzes which contained this composition, it was found that a slight residue, consisting principally of the coke employed, occasionally remained on the surfaces of the terminals in the fuze, after its discharge, and, by forming a good conducting link between them, interfered with any future effects of the magnetic current in other directions, by the establishment of a complete circuit. This obstacle to the perfect success of the composition was entirely removed by the substitution, for the coke, of another material, more easily acted on by the chlorate of potassa, and answering equally well as a conducting medium; namely, the sub-sulphide of copper. No instance has occurred in the discharge of several thousand fuzes, primed with the mixture of sub-phosphide and sub-sulphide of copper with chlorate of potassa, in which the terminals have not been found quite free from adherent residue, after the ignition.

The sub-phosphide of copper, which is produced at an elevated temperature, is a compound of very stable character, and the mixture of the three constituents is quite as unalterable as the explosive mixtures which are in general use for the preparation of percussion caps, &c. The stability of the mixture has already been submitted to very satisfactory tests. Fuzes primed with it have been found to have lost none of their delicacy and certainty, when tried more than two years after preparation.

Before passing to a statement of the results obtained by the aid of this priming composition, in investigating the extent to which magneto-electricity could be applied with certainty to the simultaneous ignition of a number of fuzes, some little account must be given of the properties of the priming material itself and of the results which regulated the proportions in which its ingredients were employed.

The sub-phosphide of copper, intimately blended with chlorate of potassa, forms a mixture in a high degree sensitive to the effect of heat, and possessed, at the same time, of some power of conducting electricity. With the employment, however, of magneto-electric machines of comparatively low power, and in cases where the resistance to be overcome by the current is considerable, this conducting property is not sufficient to ensure the ignition of the mixture by assisting the passage of the current across the interruption in the metallic circuit (*i.e.*, across the small distance between the terminals of the wires in the fuze.) It must be borne in mind that the striking distance, or the space between the terminals across which the current from even a powerful magneto-electric machine will leap, is very small. With the large lever-magnet, the spark could only be produced when the wires were almost in contact. Since, however, it is indispensable to the proper insulation of the wires in the fuze-arrangement, that the terminals should be at least one-sixteenth of an inch apart, it will be readily understood how essential to success, in operations with these machines, it is that the priming material should possess considerable conducting power. Hence the necessity of increasing the conducting power of the mixture of sub-phosphide of copper and chlorate of potassa; a result which, it has been already stated, was obtained in the first instance by the employment of finely levigated coke, and afterwards, by the substitution of sub-sulphide of copper for that substance. Many experiments were of course required to determine the proportions in which it was advisable to employ the conducting constituent, so as to facilitate the passage of the current through the mass as far as possible, without interfering too much with the sensitiveness of the explosive mixture, or producing an almost perfectly continuous connection between the two poles in the fuze, and thus promoting the passage of the current so greatly as to prevent the ignition of the composition.

Considerable difficulties were encountered in the endeavours properly to balance these conditions, when attempts were made, which will presently be mentioned, to apply the mixture in question to the ignition of several charges in circuit. The increase in the resistance of the current, consequent on the introduction of more than one interruption in the metallic circuit, necessitated an increase in the conducting power of the mixture, which it was difficult to attain, unless at a considerable sacrifice of the sensitiveness of the composition. It was consequently found that, when the proper conditions had been attained for ensuring the passage of the current through several (five or six) fuzes in circuit, the absolute certainty of the fuze, when applied in this manner, had been sacrificed. Thus, out of several fuzes tried together, which had been most carefully prepared, so as to be, as far as possible, perfectly alike, the current would ignite a few, passing through the others without affecting them; and would thus point to minute differences in the conducting powers and sensitiveness of different portions of one and the same quantity of the mixture, which, it is almost needless to observe, was prepared in such a way as to ensure the greatest possible uniformity.

By a large number of careful experiments, the proportions of ingredients were at length determined, which furnished a mixture possessed of high conducting power, attainable without detriment to the sensitiveness (ready explosiveness) of the material. The perfect certainty of its action, when applied in the fuze, to the explosion of a single charge by means of magneto-electric machines, has been proved by the ignition of at least 5000 fuzes without failure. A large number of these have been fired by means of the smaller machines already referred to.

The fuzes contrived by me for use with magneto-electric apparatus are of two kinds, the one being adapted for mining purposes and the other for firing cannon. The fuze for mining purposes (fig. 4) consists of,—

a. A head for receiving the wires which connect the fuze with the magnet and the earth;

b. Of the insulated wires, with the terminals of which the priming material is in close contact;

c. Of a small cartridge or charge of powder, enclosing the terminals, upon which the sensitive composition rests.

The wooden fuze-head contains three perforations (*a a*, *b b*, *c c*, fig. 5); the one, passing downwards through the centre, receives

Fig. 4.

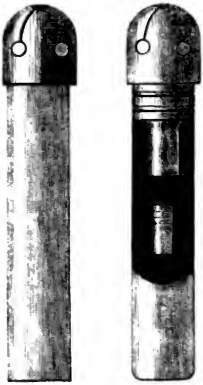
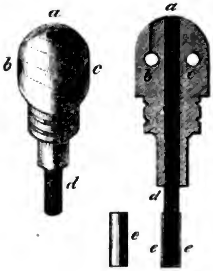


Fig. 5.



about two inches of double insulated wire, *d*.* The other two perforations, which are parallel to each other on each side of the central one, and at right angles to it, serve for the reception of the circuit-wires. The arrangement for securing the connection of these with the insulated wires in the fuzes is as follows:—

The piece of double covered wire above referred to, is originally of a sufficient length to allow of the gutta percha being removed from about one and a-half inches of the wires. These bare ends of the fine wires, which are made to protrude from the top of the fuze-head (*a*, fig. 5), are then pressed into slight grooves in the wood provided for their protection, and the extremity of each is passed into one of the horizontal perforations in the head, in which position it is afterwards fixed by the introduction into the hole of a tightly-fitting piece of copper tube, so that the wire is firmly wedged between the wood and the exterior of this tube, and is thus at the same time brought into close contact with a comparatively large surface of metal. It will be seen that it is only necessary to fix one of the circuit-wires into each of these tubes in the opposite sides of the fuze-head, in order to ensure a sufficient and perfectly distinct connection of each one of them with one of the insulated wires in the fuze.

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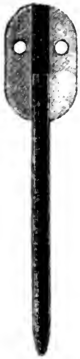
* This double covered wire consists of two copper wires of 0·022 inch diameter, enclosed side by side, at a distance of $\frac{1}{16}$ inch apart, in a coating of gutta percha of $\frac{1}{4}$ inch diameter. It has been prepared by the Gutta Percha Company for this particular purpose in considerable lengths (300 yards), from which the pieces of requisite length are cut off as required. The insulation of the two wires has been found perfect throughout the whole length manufactured at one time.

Fig. 6.



The phosphide of copper fuze for firing cannon (fig. 6) differs somewhat in construction from the mining fuze. The head is somewhat longer, and of such a form that the double-covered wires are completely enclosed in it, the lower extremity of its central perforation still remaining free to receive the top of the quill- or copper-tube, which is charged with gunpowder in the same manner as the ordinary tube-arrangement for firing cannon.

Numerous experiments made with the aid of the detonating mixture with which these fuzes were primed, established the fact that the current obtained by means even of a very powerful magneto-electric machine, when applied to the ignition of several charges arranged *in succession* in one circuit, is very limited in its powers. In illustration of this, it may be stated that, on trial being made of twenty-one consecutive sets of four charges, eighteen of the sets were perfectly discharged, but in the other three sets, only two or three of the charges were ignited. Out of five sets, of five charges each, only two sets were completely discharged; and in several attempts made to ignite six fuzes in one circuit, only four were fired in each case. In all these experiments, when charges had escaped ignition, the current had passed through the sensitive composition without firing it. When the discharged fuzes were removed, and the remaining ones properly connected, they were all fired. It has been already stated, that no beneficial effects were attained by modifying the proportions of ingredients in the priming composition, so as to diminish or increase its conducting power. Three charges might, therefore, be considered the largest number that could be ignited *with certainty* by means of a powerful electro-magnetic machine, when they were arranged in succession, in simple circuit.

The plan originally suggested by M. Savare, of arranging the charges in divided circuits was next tried, and furnished far more successful results. The simultaneous ignition of twenty-five charges, arranged as shown in fig. 2, was repeatedly effected; and forty charges were similarly exploded on several occasions. These results were all obtained with the large magnet constructed by Henley, the current being established by rapidly separating the armature from the poles by means of a lever. By a simple arrangement for shifting the connection of the main wire with the exploded charges from them to a second series, similarly arranged, twenty-five were almost simultaneously ignited on allowing the armature to return to the poles of the magnet. It was found, moreover, that the same number could be fired by means of this magnet, even if two folds of thick brown paper were interposed between the poles and the armature, so that, on depression of the lever, the armature had no longer to be forcibly detached, but simply to be removed from the magnet. The success of these results led to trials of magneto-electric machines of comparatively small size, with revolving armatures. In the employment of these machines, it was of course not expected that any single induced current obtained from them should distribute itself among a number of fuzes placed in divided circuit, as is the case with the comparatively much more powerful current obtained with the large magnet, but it was hoped that the very rapid succession of currents furnished by them would produce a very similar result, by distributing themselves over the different branches of the circuit with which the fuzes were connected, and that the ignition of the whole of the fuzes, though it could not be so positively instantaneous as when the one current was discharging the entire number, might yet be effected with such rapidity as practically to amount to a simultaneous discharge.

The results obtained fully confirmed these expectations. With a small horse-shoe magnet, 7 inches in length, 1 inch in breadth, and 1¾ inches in thickness, provided with a revolving armature and multiplying wheels, by which great rapidity of motion could be attained, twenty-five charges were fired; the effect of the discharge on the ear was, however, not like that of one single explosion, as was the case in the former experiments, but like that of an exceedingly rapid volley, in which the explosion of any single charge could not be distinguished. Still more favourable results were obtained with a very compact arrangement consisting of six small magnets, to the poles of which were fixed soft iron bars, surrounded by coils of insulated wire. The coils of all the magnets were united together so as to form, with the external conducting wire and the earth, a single circuit. An axis carried six soft iron armatures in succession before each of the coils. By this arrangement, two advantages were gained; all the magnets simultaneously charged the wire and produced the effect of a single magnet of more than six times the dimensions, and, at the same time, six shocks or currents were generated during a single revolution of the axis, so that, when aided by a multiplying motion applied to the axis, a very rapid succession of powerful currents was produced. A single large magnet with a rotating armature could not be made to produce the same succession of currents without the application of considerable mechanical power. Another peculiarity of this apparatus was that the coils were stationary, and the soft iron armatures alone were in motion: by this disposition, the circuit was never broken during the action of the machine. In the usual magneto-electric machines with rotating armatures, the circuit is necessarily broken twice during every revolution; and this frequently gives rise to irregularities in the production of the currents. By the construction adopted, the currents can never fail to traverse the circuit.

By means of this apparatus, twenty-five charges were frequently fired in divided circuit, with such rapidity that the effect on the ear was as of one explosion, only of slightly longer duration than when the large magnet was employed.

On some occasions, when a slight difference was made in the velocity with which the apparatus was worked, an interval could be distinctly noted between the first and last discharge, but even in those instances, the effect could not be considered as otherwise than a practically simultaneous discharge. Some sets of fifty charges in divided circuit were also ignited by means of this apparatus; but in those instances the interval between the first and the last discharge was naturally longer, being about the same as that observed when twenty-five charges were fired by means of the small magnet above referred to.

The system of firing charges by means of magneto-electricity, with the aid of the phosphide of copper fuze, having been thus far successfully developed, a series of experiments was instituted at Chatham, for the purpose of thoroughly testing its certainty and applicability in the field, and subsequently for ascertaining the extent to which it admitted of application to the explosion of submarine charges. These experiments extended over a period of six months, and were performed under various conditions of weather.

It will readily be understood that the best and most simple method of connecting the fuzes, enclosed in the charges, with the branch-wires and the earth, of arranging the experimental charges for explosion, and of carrying out the various small but essential details involved in the operations, were only gradually arrived at; and that, consequently, in many of the first experiments, which were only partially successful, the failures were traced to causes unconnected with the efficiency of the magneto-electric apparatus, or the fuze. It would be superfluous in this memoir to enter into details with regard to those preliminary experiments, however important they were at the period of the investigation; the description of the operations at Chatham will therefore be confined to those which were carried on according to the plan which was ultimately proved to be most efficient. The magneto-electric apparatus employed in all the field experiments was Mr. Wheatstone's arrangement of six small magnets, just now described, the whole apparatus having been enclosed in a box, so that the only exposed portions were the binding screws for the attachment of the wires, a handle for setting the armatures in motion, and a key, by the depression of which, at a given signal, the circuit could be completed.

To employ the instrument at any moment, only the following operations were necessary; the insulated wire and the copper wire passing to the earth were fixed to the apparatus by means of binding screws: the instrument was raised from the ground by being placed on its packing case; at that height, a man could operate with it when in a kneeling posture. At the signal "Ready," the handle was turned with one hand, so as to cause the armatures to revolve with the greatest possible velocity, whilst the other hand was pressed against one corner of the instrument close to the key, so as to steady the box and to be ready, at the signal "Fire," to depress the key with the thumb.

The connection of the instrument with the earth was effected as follows: a moderately clean spade was selected from among those used by the men in digging holes for the charges. One end of a piece of stout copper wire was placed under the edge of the spade, so that, when the latter was firmly forced into the ground, the wire was pressed by the earth on both sides against the iron surface. The protruding wire was wound once or twice round the bottom of the spade handle, and then attached to the binding screw of the magnet.

The gutta-percha-covered wire used in the experiments having been in occasional service at Chatham for some years, the coating had sustained some injury in two or three places. Such defects were protected from possible contact with the earth by means of waterproof cloth or sheet india-rubber. The total length of wire used was 881 yards, of which 600 were extended, lying along the ground.

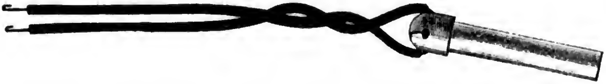
To the extremity of the covered wire a number (from 12 to 25) of pieces of similar insulated wire, varying in length between three and six yards, and serving to connect it with the individual charges, were attached in the following manner; about six inches of the extremity of the main wire and of each of the branch wires were laid bare and cleansed; the end of the former was then surrounded with those of the latter (placed in an opposite direction) and the whole tightly twisted together by means of pliers, so as to be brought thoroughly in contact with each other and with the main wire. The twisted wires were then bound round with moderately fine copper wire, which was made to bring every portion of the exterior of the bundle into connection. The joint was made rigid with pieces of stick tied against it and the whole securely enveloped in a piece of waterproof cloth or canvas, to protect it from damp and contact with the earth.

These connections, though of a very rough description and most readily prepared by any soldier, were thoroughly effectual. No instance occurred, in the whole of the experiments, of the failure of a charge, which could be attributed to an imperfect connection of its branch wire with the main wire.

The following was the method adopted for connecting the fuzes with their respective branch wires and with the earth.

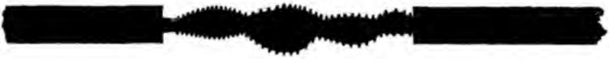
The fuzes, as they were manufactured, were always fitted with two pieces of covered wire twisted together (Fig. 7), which were tightly fixed into their proper positions by forcing a short pin of copper wire into the holes of the fuze-head. They were thus ready for insertion into the bag or other receptacle containing the charge of gunpowder, the ends of the covered wires protruding from the opening of the latter to a convenient distance for effecting the

Fig. 7.



junction with the branch- and earth-wires. The extremities of one of the fuze-wires and of a branch wire (from both of which the gutta-percha was removed to a distance of about two inches) were connected by hooking them firmly one in the other with pliers (in the manner shown in Fig. 8). A piece of fine copper binding wire was then twisted over the whole of the connection, and the joint was finally enclosed in a small wrapping of oiled canvas, in a manner similar to that adopted at the principal junction with the main wire.

Fig. 8.



The extremity of the other fuze-wire was attached to an uncovered copper wire, of sufficient length to bring the whole of the charges into connection with each other in this manner. The wire was fixed in a convenient position by being twisted round short stakes or pickets driven into the ground, and its extremities were buried in the earth, being attached either to spades, as already described, or to zinc plates about eight inches square.

The very rapid and comparatively rough manner in which these various connections were made (the tedious operation of brightening every metallic connection, so essential with the employment of the voltaic battery, being dispensed with), and their universally efficient character, were particularly commended by the officers and men who witnessed and assisted in the experiments. With reference to the earth-connections, the employment of large metallic surfaces was proved, by repeated experiments at Chatham and Woolwich, to be superfluous. The simple insertion into the ground of the uncovered extremity of the fuze-wires was found to afford a perfectly sufficient connection for ensuring the ignition of charges. The plan above described of connecting together the whole of the charges was, however, adopted as being undoubtedly the mode of proceeding least liable to accidental derangement.

The largest number of charges which it was attempted to fire at once at Chatham was twenty-five. The ignition of twelve charges was repeatedly effected, and with such rapidity as to have the practical effect of a simultaneous discharge of the whole. With twenty-five charges, the interval between the first and last discharge was very decided; it was considered, however, that even the ignition of the twenty-five charges (at a distance of 600 yards from the magnet, and with the employment of 881 yards of covered wire, and in addition, about 100 yards in the form of branch-wires) was effected with sufficient rapidity to allow of that number being employed in cases where a simultaneous discharge was required.

It need scarcely be stated that in dealing with electricity of induction, defects in the insulation of the main and branch wires had to be very carefully guarded against. Several failures in the first experiments were eventually traced to some defect of that kind. An instance even occurred, before the proper method of protecting the connections of the charges with the insulated wires was adopted, in which the deposition of moisture upon the gutta-percha-covered wire, near the charge, prevented the ignition of the latter, by forming a connecting link between the extremity of this wire, where it was exposed and attached to the fuze, and the uncovered wire leading to the earth, in consequence of the two wires being in contact at a distance of several inches from the fuze. It is therefore always a preliminary precaution of primary importance, that the insulating covering of the wire to be employed be carefully inspected, while the latter is being laid out for use, and that any imperfections be protected from possible contact with the earth, or from the access of moisture; a result easily attainable by the application of some waterproof envelope to the injured portion.

The experiments instituted at Chatham with the object of applying the magneto-electric current to the ignition of *submarine* charges were attended with greater difficulties than those which served to test the system in its application to land-operations; nevertheless, the results ultimately attained were also of a character to lead to definite and favourable conclusions.

The method of establishing the connections of a charge with the wire and the earth differed naturally in some respects from the mode of proceeding already described. The charges of powder were contained in canisters of block tin carefully soldered so as to be watertight.* The fuze, with two wires attached as before, the one a few inches longer than the other, was inserted into the charge, and fixed in its proper position in the canister by means of a

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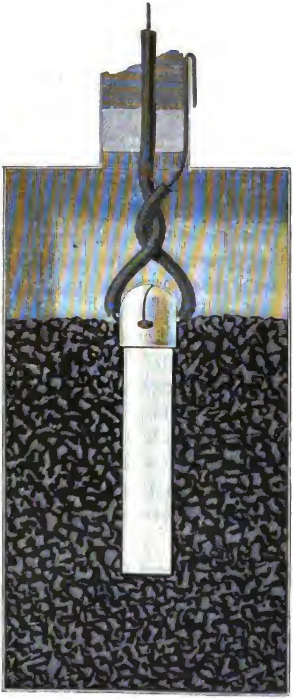
* Any vessels of this material, such as turpentine cans, may be employed, provided they be perfectly coated inside with marine glue, or some other description of varnish.

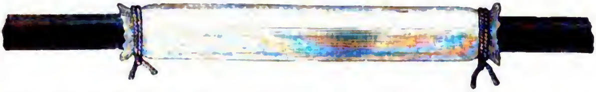
Fig. 9.



loose fitting bung (see Fig. 9) pushed a little distance into the neck, and cut out on one side, so as to admit of the passage of the longer insulated wire, while the bare part of the shorter wire was firmly pressed by the cork against the inside of the neck. The latter was then completely filled up with melted gutta-percha, and the extremity of the short uncovered wire was bent back over its side, so as to be in close contact with the metal surface. In this manner, the enclosed fuze was brought into good metallic connection with the wet earth, or water, by which the canister was surrounded.

The insulated wire, projecting from the mouth of the canister, was connected with one of the branch wires in the manner already described; but in order thoroughly to protect the connection from the water, in which it would become immersed, a piece of vulcanized India-rubber tubing, of suitable length, and a tin-tube, rather longer and wider than the latter, were slipped on to the branch-wire before it was joined to the fuze-wire, and, when the junction had been effected, the India-rubber tube was pulled over it, and tied very firmly at both ends on to the gutta-percha covering of the wires. (Fig. 10).

Fig. 10.



A small quantity of a cement (consisting of bees-wax and turpentine) was rubbed in between the latter and the ends of the India-rubber tube, so as thoroughly to ensure the exclusion of water, and finally the tin-tube was pulled over the joint, and fixed (by compressing the ends) for the purpose of imparting rigidity to the junction, and thus protecting it from injury by any sudden twist or strain. By these arrangements, when carried out with moderate care, the perfect exclusion of water from the charge and from its connection with the branch wire was effected.

The first trials of these charges were made in a shallow canal with a mud bottom, and from which at the time of experiment the water was receding so rapidly, that before the whole of the charges had been immersed, several of them were exposed to view, being partly imbedded in the mud. Twenty-five charges were arranged, of which thirteen were exploded, though less rapidly than in the experiments on land. On the next occasion, when twenty-five charges were entirely surrounded by water (simply resting upon the firm bed of a pond of some depth), only four of the charges were exploded. Several other attempts were made to fire a smaller number of (ten and five) charges similarly immersed, but in every instance only four were ignited. A careful examination into the cause of the invariable explosion of so comparatively limited a number of charges under water, led to the following explanation:

It will be remembered that the explosion of numerous charges in a divided circuit by the magneto-electric apparatus with revolving armatures is effected by the action of an exceedingly rapid succession of currents. The rapidity with which they follow each other, however great, cannot equal that with which the terminals of a fuze, enclosed, in a small charge, under water, come into contact with the latter after the explosion. The instant this occurs, a complete circuit is established through the water, and any further action of the current is at once arrested. By the time, therefore, that four charges had been ignited in extremely rapid succession, so as to be apparently exploded at once, a sufficient interval of time had in reality elapsed to allow the water to re-occupy the space filled for a brief period by the gaseous products of the first explosion, and thus to rush in upon, and complete the circuit with, the terminals of the fuze. It appears probable that, with the employment of larger charges of powder (about eight ounces was the quantity exploded in each charge) when the volume of water displaced by the explosion would be more considerable, a great number of charges would be exploded before the circuit could be completed by the water. No opportunity occurred during the experiments of ascertaining this by actual trial.

The instances, however, in which it is indispensably necessary that a number of charges should be exploded together, suspended in water, or simply resting on the ground below, and being in immediate contact on almost all sides with water, appear to be of exceptional occurrence. Submarine charges are generally so arranged as to be partially or completely surrounded by the objects upon which the force of the exploding charge is to be exerted, and they are even frequently firmly fixed in their position by being partly or wholly embedded in sand, mud, or some similar material. In such cases, the resistance to be overcome by the explosion is greater than if, under conditions otherwise similar, the charges were simply in direct contact with the water, and hence the interval is increased which must elapse before the water can complete the circuit.

The results of some experiments made at Chatham appear to show that, under such circumstances, the number of charges ignited at one time by the magneto-electric apparatus must be greater than if they were simply immersed in water. One experiment has already been mentioned, in which thirteen charges out of twenty-five were exploded at one time, most of them being imbedded in mud. On another occasion ten charges were placed in small pits filled with water, the canisters being covered in with mud beneath the latter. Nine of the charges were fired; the branch wire of the tenth was accidentally severed at the moment of the explosion, from its lying across one of the pits.

A careful consideration of the results furnished by these and other similar experiments, on the application of magneto-electricity to the explosion of charges, led to the following conclusions:

The explosion of a single charge of powder by means of the phosphide of copper fuze and a magneto-electric apparatus (even of the smallest size generally manufactured) is absolutely certain.

With the employment of a magneto-electric apparatus similar to that used in the Chatham experiments, and termed by Mr. Wheatstone the "magnetic exploder," the ignition at one time, of fuzes varying in number from two to twenty-five, is certain, provided these fuzes are arranged in the branches of a divided circuit in the manner described. To attain this result, it is only necessary to employ a single wire, insulated by a coating of gutta-percha or India-rubber, and simple metallic connections of the apparatus and the charge with the earth. The explosion of from twelve to twenty-five charges may be effected in the above manner, at a distance of at least 600 yards from the apparatus, with a rapidity which in its results will in all probability have the practical effect of a simultaneous discharge. This statement refers only to charges on land. The number of submarine charges which can be exploded with certainty at one time by means of the magnetic exploder appears more limited;. but if such charges are entirely or partially embedded in sand, mud, or other dense materials, from two to ten may be fired with certainty. By the employment of separate wires, leading from the instrument to each charge, or by adopting a rheotomic arrangement for effecting the discharge, there is little doubt, however, that the results obtained with the magnetic exploder in submarine operations would be quite equal to those definitely established in the ignition of charges on land.

The only precaution to which it is necessary to attend, in order to ensure uniform success in the application of the magnet, are the proper insulation throughout of the main wire and branch wires leading from the instrument to the charges, and the thorough protection of all connections of wires from the access of moisture.

The system of firing charges by magneto-electricity possesses important advantages over the application of the voltaic battery to that purpose, the principal of which are as follows:

The magnetic exploder is at any time ready for immediate employment; it is easily transported by hand, being of small dimensions and weight; it is not liable to injury or derangement provided the most ordinary care be applied to its preservation and transport; it may be employed for many years without suffering any important diminution of its power; and, as all arrangements in connection with the instrument are mechanical, any injury which they may sustain can be repaired by ordinary workmen.

The magnet-fuze is more certain than any fuze-arrangement applied with the voltaic battery, and as safe as any arrangement employed for igniting gunpowder by friction or percussion. It may be preserved for a great length of time in any climate, and will bear very rough treatment without chance of injury.

The implements and materials required for carrying on operations with the magnet, in addition to the instrument, the wire and the fuzes, are very few in number, inexpensive, and easily replaceable; they occupy but little space, and require no more care in their transport than ordinary artisan's tools.

All the operations necessary in the employment of the magnet (the connection of the fuzes with the instrument, their introduction into the charges, and the explosion of these), are of the simplest possible character, and can therefore be performed by any person of ordinary intelligence.

It can be confidently affirmed that the general certainty of the magneto-electric arrangement is decidedly greater than that of voltaic batteries, and that the necessity of ensuring a proper insulation of wires and connections, though it may be regarded in the light of a difficulty by those accustomed to carry on operations with the voltaic current, is in reality a condition which may be fulfilled readily and with certainty by the use of very simple means and precautions.

There is little question that, with battery-power of great magnitude, and with the successful fulfilment of the numerous indispensable conditions and precautions (which long experience has shown to be involved in considerable uncertainty), it is possible to fire at one time a very much larger number of charges than those which have been quoted as the greatest task to be accomplished with certainty by the apparatus proposed for general use. It has, however, been stated by high military authorities on these subjects, that the instances in which it is required to fire more than from twelve to twenty charges at one time are quite exceptional, and that indeed, twelve may be considered as the greatest number of charges which it may be necessary to apply in all general operations.

In special cases, such as the destruction of very massive works, where it would be advantageous to apply the force of exploding gunpowder simultaneously to a very large number of different places, the employment of arrangements of a special character is always admissible. In such circumstances, there is no question that a powerful induction coil-machine, with the employment of very moderate battery-power, and of the new fuzes, would furnish with certainty, results of as great a magnitude as could be desired, and that its use would be less likely to be attended with difficulties than that of the hydro-electric or plate electric machine.

For all operations of a general character, however, the results obtained up to the present time, have satisfactorily proved that the system of exploding charges, in the form of mines, for the simultaneous or regularly successive discharge of guns at a considerable distance, or for any similar purpose, by a magneto-electric current is, in point of certainty and simplicity, superior to any other which has hitherto received application.

XVI.—*On the Composition of a Carbonaceous Substance existing in Grey Cast Iron.*

By F. Crace Calvert, F.R.S., F.C.S.

Having often noticed that the quantity of carbonaceous mass left in the vessels in which grey cast iron was dissolved, varied with the concentration of the acid used, I began in September, 1858, a series of experiments on the action of very weak acids on cast iron, in the hope of obtaining a quantity of the so-called graphite which it contains, and I believe that I have arrived at results which throw much light upon the chemical composition of this substance, proving it to be composed of iron, carbon, nitrogen, and silicium. This substance occupies exactly the same volume as the cast iron from which it is obtained, and is sufficiently soft to be easily penetrated by a blade. I shall now describe the method of experimenting.

Cubes, of one centimetre in dimension, of Staffordshire cold-blast cast iron were placed in corked bottles with eighty times their volume of the following weak acid solutions:—

Sulphuric	acid,	1	alkalimeter	contained	10	grains of	SO_3	anhydrous.
Nitric	„	1	„		13·5	„	NO_5	„
Hydrochloric		1	„		9·12	„	HCl	„
Acetic	„	1	„		12·75	„	$C_4H_3O_3$	„
Oxalic	„	1	„		9·00	„	C_2O_3	„
Tartaric	„	1	„		33·00	„	$C_8H_4O_{10}$	„
Gallic	„	1	„		10·00	„	cryst. acid.	

The foregoing figures represent the equivalent quantity of anhydrous acid as compared with 10 grains of anhydrous sulphuric acid per alkalimeter.

Besides the above, phosphoric, carbonic, oleic acid, tannin, and acid peat-water were also used.

After three months of contact, I found that, although the external appearance of the cubes was not changed in any of the vessels, still those in contact with the weak sulphuric, hydrochloric, and acetic acid solutions, especially the latter, had become so soft externally that the blade could penetrate three or four millimetres into the cubes. I, therefore, removed the solutions from the vessels and replaced them by an equal bulk of each weak acid solution, and continued to do so every month for two years.

I then found that the cubes in contact with the acetic acid ceased to yield iron to the acid, although they were still of the original size; they had, therefore, become transformed into the carbonaceous substance before mentioned. These are the results of the action of the various weak acid solutions, on the centimetre cubes of grey cast iron, after two years :—

Acetic acid . .	Complete.
Hydrochloric acid .	Nearly complete.
Sulphuric acid .	Ditto ditto.
Nitric acid . .	Action less complete than above.
Phosphoric acid .	No similar action.
Oxalic acid . .	Ditto.
Tartaric acid . .	Ditto.
Tannin . . .	Very slight action.
Carbonic acid .	Ditto.
Gallic acid . .	Ditto.
Oleic acid . .	Ditto.
Acid peat-water .	No similar action.

The action of acetic acid on grey cast iron is most interesting; for instead of ceasing when saturated with oxide of iron, as is the case with other acids, its action is continuous, if the precaution is taken to close the mouth of the vessel with an ordinary cork. Thus I have had cubes of cast iron in contact with the same quantity of acetic acid for two years, and the chemical action still existed when the contents of the bottles were examined. This action of acetic acid appears, therefore, to be analogous to that which it has on lead.

To examine the chemical composition of the cubes transformed by the action of acetic acid, they were reduced to fine powder in an agate mortar, and well washed with boiled water slightly acidulated with acetic acid. The powder was then dried at 115° C., in a dry atmosphere of carbonic acid or hydrogen, according to the nature of the body to be determined in the mass. The carbonaceous substance so prepared presented the following properties and composition :—

The cubes of grey cast iron, which originally weighed 15·324 grammes weighed only 3·489 at the end of the two years, and their specific gravity was reduced from 7·858 to 2·751. Their composition was as follows :—

	Composition of the original cubes.	Composition of the carbonaceous substance.
Iron . .	95·413	79·960
Carbon .	2·900	11·020
Nitrogen .	0·790	2·590
Silicium .	0·478	6·070
Phosphorus .	0·132	0·059
Sulphur .	0·179	0·096
Lost . .	0·108	0·205
	100·000	100·000

These results lead to the following remarks :—

Nitrogen.—That the largest part of the nitrogen originally existing in the cast iron remains in the graphitoid substance, and only a small portion is transformed into ammonia. These facts tend to prove that the nitrogen of cast iron exists in it under two states, namely, that one portion is combined with the carbon, whilst the other is in a condition to unite with the hydrogen liberated from the water, and thus to form ammonia. This method of ascertaining the amount of nitrogen in cast iron, by determining the quantity of nitrogen in the state of ammonia, and that existing in the carbonaceous mass, appears to be the best process known, for I obtained 0·790 from the same cast iron which only yielded me 0·100 by the process lately published by M. Fremy. For ordinary analyses of cast iron, the slow action of acetic acid may be advantageously replaced by that of hydrochloric acid, taking care to use freshly distilled acid, water free from ammonia, and placing the whole in a flask provided with cork and tube, so as to exclude the possibility of the ammonia existing in the atmosphere from interfering with the experiment. By this means the amount of nitrogen existing in cast iron can be easily and speedily ascertained.

Silicium.—I have ascertained by direct experiments that it is silicium, and not silica, that enters into the composition of the carbonaceous mass. Amongst other experiments I may state that I took 5·96 grains of the carbonaceous substance dried at 115° C. in a current of carbonic acid, and after having placed it in a small platinum dish, the whole was introduced into a porcelain tube, and submitted for several hours at a red heat to a current of pure and dry oxygen. I then found that the 5·96 grains had increased to 7·39 grains, or nearly the theoretical amount: for 5·96 grains of substance would lose 0·664 of carbon, and the remaining 0·338 of silicium would become 0·718 of silica, whilst the 4·692 of iron would become 6·702 of peroxide of iron, or both added together 7·420, being within 0·13 grain of the weight actually found. Now, if the iron in the mass had been in the state of protoxide, and the silicium in the state of silica, the 5·96 grains employed would, after the loss of carbon, have decreased to 5·551 grains, leaving, therefore, no doubt that the carbonaceous substance contained metallic iron and silicium. Finding, however, that the quantity of silicium in the carbonaceous substance, though high, did not represent the whole of the silicium contained in the cast iron employed, I passed the hydrogen liberated by the action of weak acids on cast iron through fuming nitric acid, and found, on the evaporation of this acid, a white deposit of silica. All acids which give off hydrogen when in contact with cast iron, also give rise to the gas discovered by Wöhler, namely, silicide of hydrogen.

Carbon.—Like silicium, the quantity of carbon found in the carbonaceous compound does not represent the whole of the carbon pre-existing in the cast iron employed, as carburetted hydrogens are given off during the slow action of acetic acid on cast iron.*

Iron.—As shown by the above analysis, the carbonaceous compound contains 79·960 of metallic iron, even when the acetic acid has ceased to act upon it. I have made several experiments to satisfy my mind that the carbonaceous mass contains metallic iron, and not oxide of iron. Thus, I passed hydrogen, at a dull-red heat, over some of the carbonaceous substance previously dried at 115°, and obtained no water, and the experiment related under the head of silicium confirms this conclusion. All grey cast irons appear to yield the same relative proportions of carbon and iron; but as cast iron becomes harder and whiter, the amount of carbon decreases, and, in fact, nearly disappears in Welsh white cinder iron, being replaced by silicium. The relative amount of carbon and iron in the carbonaceous substance corresponds to 4C and 6Fe, or are the same that I have found in some cast iron which had been saturated with carbon, by melting No. 1 cast iron in presence of a large excess of coke on a cupola, and called technically "keechy."

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* I am now engaged in preparing a sufficient quantity of these hydrocarbons to enable me to submit them to a careful examination.

I do not, however, believe that the carbonaceous substance obtained by me is simply composed of 4C and 6Fe, but that the nitrogen and silicium found in it must likewise enter into its composition. But, in the present state of my researches, it would be premature to attempt to assign any definite composition to this substance. As I am, however, still pursuing the subject, I shall be happy, if I arrive at any conclusion, to communicate the same to the Society.

When the *graphitoid* substance prepared by the above process, is exposed to the atmosphere, it absorbs oxygen with rapidity, and the temperature of the mass rises rapidly, protoxide of iron being first formed, which is converted into sesqui-oxide; but when this mass is placed in distilled water, a chemical action ensues similar to that described by M. Kuhlmann, namely, a portion of the carbon is converted into carbonic acid by the oxygen of the sesqui-oxide of iron, and the carbonic acid thus produced unites with protoxide of iron to form carbonate of protoxide of iron. The atmospheric action on the carbonaceous substance above described explains the difference of composition which I have found to exist between the body obtained by me, and that of a soft graphitoid mass which was found to replace a mass of iron buried for many years amongst coal cinders, and which had the following composition:—

Mean of several Analyses.

Peroxide of iron	66·61
Carbon	12·03
Silica	18·13
Sulphur	0·79
Phosphorus	traces
Lime	2·14
	99·70

Nitrogen was also present, but its amount was not determined.

I am aware that the latter curious and interesting change in cast iron has been several times noticed. Thus, Dr. Henry published a short notice on this subject in the "Annals of Philosophy." Mr. R. Mallet also described a similar substance in the "Transactions of the British Association." Mr. Warington has also noticed the conversion of cast iron into a soft black substance which occurred in a brewery where it was in contact with sour beer. Lastly, Mr. E. W. Binney records, in the 11th volume of the "Memoirs of the Manchester Philosophical Society," a description of a similar substance found by him at the emptying of a deep coal-pit, in which the cast iron had remained submerged for a few years, and which yielded to Dr. Angus Smith the following composition:—

Iron and bases	38·8
Carbon	40·0
Silica	19·7
	98·5

In conclusion, the conversion of the guns of the "Royal George," at Spithead, is so well known, that I merely refer to it to express the same opinion as Mr. Binney,—that it strongly behoves those who have charge of lighthouses, now so often erected in the sea upon cast-iron pillars, to carefully and frequently inspect such structures, for day by day their support must be weakened by the action of the salt-water. (See Memoirs of "Manchester Philosophical Society, Vol. II., page 28.)

XVII.—*On the Bromide of Carbon.*

By Arthur E. W. Lennox.

The compounds of carbon with bromine have as yet received but limited attention. The tetrabromide of carbon—CBr_4 of the methyl series—is altogether unknown. Kolbe failed in obtaining this compound by submitting disulphide of carbon, at a high temperature, to the action of bromine; and I learn from Dr. Hofmann, that the action of pentabromide of antimony on the disulphide gives no better result. The bromide of carbon C_2Br_4, has been obtained by Lœwig*, who procured this substance by the action of bromine on alcohol or on ether, when it is formed according to the equations—

$$C_2H_6O + 4Br_2 = C_2Br_4 + 4HBr + H_2O.$$
$$C_4H_{10}O + 8Br_2 = 2C_2Br_4 + 8HBr + H_2O.$$

These processes appear, however, to be attended with difficulties. At all events, Vœlckel†, who repeated Lœwig's experiments, failed in obtaining the substance described by that chemist.

A simpler method for obtaining this bromide of carbon appeared to present itself in the perfect substitution of bromine for the hydrogen of olefiant gas.

The brominated derivatives of ethylene have been chiefly examined by Regnault and by Cahours, and, more recently, by Wurtz and by Sawitch. The following terms have been obtained:—

Dibromide of ethylene	$C_2H_4Br_2$.
Dibromide of monobrominated ethylene .	$C_2(H_3Br)Br_2$.
Dibromide of dibrominated ethylene .	$C_2(H_2Br_2)Br_2$.
Dibromide of tribrominated ethylene .	$C_2(HBr_3)Br_2$.
Monobrominated ethylene . . .	C_2H_3Br.
Dibromated ethylene	$C_2H_2Br_2$.

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* Ann. Ch. Pharm., iii, 292.

† Ibid., xli, 119.

It thus appears that the whole series has been obtained, with the exception of the tetrabrominated ethylene, which would be the bromide of carbon obtained by Lœwig in the reaction above indicated.

Of the brominated derivatives of ethylene, dibromide of ethylene, monobrominated ethylene (bromide of vinyl), and dibromide of monobrominated ethylene, have as yet been best investigated. In re-examining these substances, in transforming dibromide of ethylene, by the action of an alcoholic solution of potash, into monobrominated ethylene, and the latter, by treatment with bromine, into the corresponding dibromide, I had an opportunity of tracing, step by step, the observations of my predecessors.

The action of an alcoholic solution of potash upon the dibromide of monobrominated ethylene yields, together with secondary products, a comparatively small quantity of the oily compound $C_2H_2Br_2$, which is still further diminished by the extraordinary property exhibited by this substance of undergoing a molecular transformation similar to that of dichlorinated ethylene, as observed by Regnault,* and of monobrominated ethylene, more recently examined by Dr. Hofmann.† Dibrominated ethylene having been lately the subject of a more minute investigation by M. Sawitch,‡ I have not entered upon a more close examination of this body, but have at once, by the renewed action of bromine, converted it into the

Dibromide of Dibrominated Ethylene.

Bromine attacks the dibrominated ethylene with the greatest energy, heat is evolved, and the bromine disappears. When the bromine was no longer fixed, the orange-yellow liquid was treated with a weak solution of potash, washed with water, and ultimately distilled with precaution. It boils at about 200° C., but not without partial decomposition, white fumes containing hydrobromic acid being given off during ebullition, which powerfully and persistently attacked the eyes.

The bromine-compound is insoluble in water, but dissolves readily in alcohol and in ether; when exposed to a freezing mixture it solidifies to a white crystalline mass. As it was found impossible to purify this substance for analysis by distillation, a current of perfectly dry carbonic acid gas was passed through the liquid heated in a water-bath to about 75° C. After a time it assumed a lighter colour, and no longer gave off hydrobromic acid.

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* Ann. Ch. Phys. [2.] lxix, 151.

† Chem. Soc. Qu. J., xiii, 68.

‡ Bulletin de la Société Chimique de Paris, 1861, p. 7.

047·0 grm. of substance burnt with lime gave 1·016 grm. of bromide of silver.

The formula.

$$C_2\,H_2\,Br_4$$

requires the following values.*

	Theory.		Experiment.
C_2	24	,,	,,
H_2	2	,,	,,
Br_4	320	92·40	91·97
	346		

Tribrominated Ethylene.

The dibromide previously described is powerfully acted upon by an alcoholic solution of potash:

$$C_2H_2Br_4 + KHO = C_2HBr_3 + KBr + H_2O.$$

Addition of water to the alcoholic solution precipitates the tribrominated ethylene as an oily substance, boiling at 130° C, which, by digestion over chloride of calcium and subsequent careful distillation, may be obtained sufficiently pure for analysis.

0·342 grm. of substance burnt with lime, furnished 0·726 of bromide of silver.

The formula,

C_2HBr_3 requires,

	Theory.		Experiment.
C_2	24	,,	,,
H	1	,,	,,
Br_3	240	90·56	90·32
	265		

Tribrominated ethylene, like the other substitution-product of ethylene, is apt to furnish an isomeric solid, which is readily soluble in alcohol and in ether, from which it crystallises in colourless plates. On slowly evaporating a solution of the oily modification in alcohol or ether, the crystalline solid is likewise obtained.

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* H = 1; O = 16; C = 12; Br. = 80.

Dibromide of Tribrominated Ethylene.

To obtain this compound, tribrominated ethylene was introduced into a retort, and cautiously distilled into a receiver containing bromine. Combination took place with considerable evolution of heat. The orange-yellow liquid thus produced was washed with weak potash, and ultimately with water. Thus purified, this bromine-compound is a yellowish red oil, soluble in alcohol and ether, and solidifying when exposed to a frigorific mixture. I have not succeeded in preparing this substance in a state of sufficient purity for analysis; but its nature is sufficiently established by the facility with which it is transformed into tetrabrominated ethylene, or bromide of carbon, by the action of alcoholic solution of potash.

Addition of water to the alcoholic solution precipitates this compound as an oily liquid, which, when slowly deposited by spontaneous evaporation from its solution in alcohol or ether, separates in beautiful crystalline plates of an agreeable aromatic odour and burning taste: one or two crystallisations render it perfectly pure. It is heavier than water; fuses at 50° C; sublimes at a higher temperature; and is not attacked by the mineral acids. These properties identify this compound with the bromide of carbon which Lœwig obtained by the action of bromine upon alcohol and upon ether. For analysis it was dried over sulphuric acid in vacuo, and has furnished the following results.

0·315 grm. of substance burnt with a mixture of oxide of copper and chromate of lead gave 0·078 carbonic acid.

0·175 grm. of substance burnt with lime gave 0·330 grm. of bromide of silver.

The formula,

$$C_2Br_4$$

requires the following values.

	Theory.				Experiment.
C_2	24	..	6·98	.. ..	6·69.
Br_4	320	..	93·02	.. ..	92·57.
	344				

The tetrabrominated ethylene is generated by the action of an alcoholic solution of potash upon the dibromide of tribrominated ethylene, according to the following equation:

$$C_2HBr_5 + KHO = C_2Br_4 + KBr + H_2O.$$

The experiments which form the subject of this note were performed in the laboratory of Dr. Hofmann.

XVIII.—*On the Power ascribed to the Roots of Plants of rejecting Poisonous or Abnormal Substances presented to them.*

By CHARLES DAUBENY, M.D., F.R.S., M.R I.A., Foreign Associate of the Royal Academy of Munich, &c., and Professor of Botany, Oxford.

BEFORE reporting to the Society the results of a few experiments which I have lately made on the subject of the absorption of mineral bodies by the roots of plants, it may not be amiss for me to enter into some general account of the state of our knowledge relative to the subject referred to, including a brief notice of the experiments tending to elucidate it, which have been already communicated to the public by myself and others.

I may in the first place remind you, that, with regard to the functions of the roots, two opposite views have been entertained: the one, that they consist simply of a system of cells, surrounded by membrane, which possesses no peculiar properties, but is capable, by virtue of endosmose, of absorbing any fluid that happens to lie in contact with their external surfaces, and, by the force of capillarity, of transmitting the same afterwards to the parts above: the other, that as vital organs, they are endowed with a certain power, which seems to us analogous to selection, or, at least, answers the same purpose; in consequence of which they abstract from the fluid presented to them those principles which are required for the general uses of their own economy and that of the plant in general.

The former, doubtless, is the more readily intelligible hypothesis, and is one in support of which many facts may be alleged.

Saussure, for instance, found, that when the roots of a water-plant, such as the *Polygonum Persicaria*, were immersed in water containing equal quantities of various saline and other soluble bodies, the latter were absorbed, not in the ratio of their respective fitness for supplying the wants of the system, but in proportion to the facility with which the solution was capable of entering the spongioles, and of flowing through the tissues of the plant.

Gum and humus, for instance, being viscid, entered the spongioles in much smaller quantity* than various saline bodies did, which might be regarded as less needed by the plant which absorbed them.

But, of all those tried, no one was taken up in such large quantities as sulphate of copper; a circumstance which may be attributed to the poisonous and corrosive quality of this substance, owing to which the texture of the cells became disorganized, and the entrance of the solution into the vegetable texture took place as freely, perhaps, as if the parts had been actually severed asunder.

These statements of Saussure were confirmed by Sir Humphry Davy, who, in his "Agricultural Chemistry," pointed out, that saline solutions are absorbed more readily when in a diluted state than when concentrated.

Later experimentalists have even gone so far as to contend, that, with the exception of such salts as those of copper, which destroy the texture of the roots, all solutions are absorbed with equal readiness. Such was the conclusion arrived at by Dr. Lindley, from researches of his own, which are detailed in vol. XVIII of the "Annals of Natural History."

The experiments of Boucherie have also been appealed to, as affording an argument from analogy in support of this same view. In these, openings were made in the lower part of the trunks of various trees by sawing out a portion of the wood, and a water-proof bag was placed round the severed portion, so that a saline solution might be introduced, which was rapidly absorbed by the tree, of whatever nature it might be.† Through this device, wood became impregnated with various metallic salts, by which its hardness and durability are augmented in a remarkable degree.

Similar experiments have been instituted by Mr. Hyett, of

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* The late researches of the Master of the Mint on endosmose may serve to explain this, on the principle that gelatinous bodies do not pass through membrane.

† Annales de Chemie, vol. lxxiv, p. 113.

Painswick House, near Gloucester, the results of which are given in vol. VIII of the "Transactions of the Highland Society," published in 1843.

The same inference has been deduced from observations made as to the influence exerted upon the constitution of a plant by the quality of the soil, or by the nature of the ingredients present in it which are submitted to its roots.

This influence was shown by the experiments of Saussure, where a fir, which had grown at Mont Breven on a dolomitic rock, was proved, when burnt, to contain, in its ashes, a certain percentage of magnesia; whilst the same species from Mont la Salle, a granitic rock, was destitute of magnesia, but possessed an equivalent increase in the lime and potassa belonging to it; and likewise from those of Berthier, showing, that the ashes of a fir which had grown in Norway, yielded only 16·8 per cent. of alkalies, 29·6 of lime, and 3·3 of magnesia, whereas the same kind of timber from Allevard, in France, afforded 34·7 of alkali, 13·6 of lime, and 4·35 of magnesia.

Such are the principal facts that may be appealed to in support of the hypothesis, that roots are merely passive instruments, which take up whatever is presented to them without selection or preference.

It must, however, on the other hand, be observed, that the properties of endosmose, capillarity, and the like, to which the absorption of saline fluids by the roots, and their transmission through the stem, may be attributed, are common to all tissues similarly constituted, whether dead or living; and that the co-existence of other properties more especially vital, is by no means excluded by their presence.

It is just the same, indeed, with the animal kingdom. No one doubts, that the living organism of animals is amenable to the common laws of matter, however much the latter may be controlled, and masked, as it were, by the forces of life.

That in the case of the spongioles also, similar functions dependent upon vitality must be assumed to be superadded to those common to matter generally, may be argued from the fact, that the power of substituting one ingredient for another is at any rate circumscribed within very narrow limits.

The most trustworthy experiments hitherto made appear to show: 1st. That it is impossible to replace any of the bases or acids which usually enter into the composition of the vegetable by any other of the same series which are not usually present: 2ndly, That even those bases which are capable, to a certain extent, of replacing each other, cannot do so indefinitely: and, 3rdly, That much of the difference in composition which has been remarked as existing between plants of the same species, growing in different soils, or manured in various ways, may be accounted for by the predominance of one or other of its proximate principles in the several samples submitted to examination.

Thus wheat cultivated in one soil, may contain more gluten and less starch than in another, and hence the chemical constitution of the grain must in each instance necessarily vary.

In support of these positions, I will appeal to some experiments of my own already published, as well as to those of others; and I will also allude to certain facts of general notoriety which seem to me to point in the same direction.

In the Transactions of the Linnæan Society, vol. XVII, published in 1835, I showed, that plants watered with a solution of nitrate of strontia, and seeds sown in soils containing the sulphate of the same earth, never appeared to absorb any portion of this base: for it could not be detected in their stems, leaves, or flowers, and only in the minutest quantity in, or attached to, their roots.

In relating these experiments, I took the opportunity of alluding to an analogous result obtained by myself with reference to the animal kingdom, where hens, allowed access, during the breeding season, to sulphate of strontia, but to no other earth, laid eggs with soft shells.

I may also appeal to the notorious fact, that no acid can replace the phosphoric in the vegetable organism; a principle upon which the entire theory of scientific agriculture, as expounded by Liebig and others, seems to be based. Were this not the case, the necessity of supplying, from time to time, the mineral phosphates, as fast as they are drawn off by successive crops, might be superseded by other expedients. Some interesting experiments, bearing upon this subject, are reported on the authority of the Prince of Salm Horstmar, in the Annales de Chimie, for 1850, vol. XXXIII. The Prince moulded some little wax vessels, in height about 2¼ inches, and in diameter 1 inch, and filled each of them either with pure sand, or with powdered rock-crystal which had been previously calcined. Into these vessels were introduced a few grains of oats, and along with them a minute quantity of one or more of the ingredients which, by analysis, this plant has been found to contain.

The following were the results arrived at:—

1. When neither any inorganic nor nitrogenised materials had been added, the oats sprouted, but came up weak, and were reduced to two flowers and a single fruit.

2. When nitrogenised substances were added, the plant shot up higher, but was too feeble to sustain itself in an erect position.

3. When denied access to nitrogenised materials, but supplied with all the inorganic principles normally present in it, namely, with silica, potassa, lime, magnesia, and oxide of iron, together with phosphoric and sulphuric acids, the plant was small and languid, and whilst the formation of flowers took place to a more limited extent than in the former case, that of grain was altogether wanting.

4. When both the mineral substances above enumerated and the nitrogenised matters were present, there was an increase both in the vigour of the plant and in the number of its flowers; but still something appeared to be wanting in the pulverized quartz, which existed in the river sand; for, although lateral shoots were produced, showing a power of development to reside in the plant, still the regular formation of grain did not take place.

5. But when any one of the above seven inorganic substances was wanting, its development became in some way or other arrested.

Thus when magnesia was not supplied, the growth of the plant was feeble; when potassa, it was stunted, and only a single stem produced; when soluble silica, the growth of the stem was arrested; when phosphoric acid, only one flower was obtained, and this did not produce grain; when sulphuric acid was not supplied, there was no stem, and the plant died before the third leaf had been produced; and when iron was wanting, the plant was deficient in its natural green colour.

The experimental results above obtained are decidedly adverse to the idea, that even normal substances can replace each other indefinitely in the structure of a plant, showing, as they seem to do, that the constituents are all of them indispensable to their healthy growth.

The fourth conclusion indeed arrived at, namely, as to the imperfect development of a plant grown in powdered quartz, even where all the bodies known to be essential to it are provided; although it arrives at a perfect state of maturity, in all respects, when grown in river sand, seems to indicate, that we are still unacquainted with all the ingredients of the soil and of the plants grown in it.

This is the point, therefore, towards which our inquiries should be directed, and which the Prince himself, at the end of his Memoir, proposes to investigate. As, however, ten years have since elapsed without any further communication from him having reached my knowledge, I conclude that we must not expect any further elucidation of the subject from this quarter.*

In the interval, however, the remarkable researches of Bunsen and Kirchhoff, on Spectrum Analysis, have established the existence in nature of some substances hitherto unsuspected, and the wide diffusion of others hitherto regarded as of great rarity; so that, as I perceive has been already suggested by Dr. Cameron in a paper read before the Dublin Society,† the failure of our crops may, in certain cases, be owing to the absence from the soil of some ingredient hitherto overlooked, such for instance as lithium, or the new alkali-metal cæsium, which had been withdrawn by preceding crops, and not restored by the species of manure which had been subsequently applied.

If then, it be true, that abnormal substances cannot supply the place of normal ones, and, therefore, do not enter into the organisation of a plant, we have only the alternative of supposing, that when brought into contact with the roots, the former either are not admitted at all into the system, or are afterwards excreted from it.

Of the two, the former would seem to be the more legitimate inference; for if these bodies had been excreted, we ought to find traces of them *in transitu* distributed throughout the various tissues of the plant.

The latter is, indeed, actually found to be the case, when substances of this nature are brought into contact with the cut surfaces of the stem or roots, as in the experiments of Boucherie; or even when the vitality of the root is destroyed by the application to it of a poisonous or corrosive substance, as in the cases reported by Saussure.

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* Since the reading of this Paper, I have found, from a late notice in the Chemical News, copied from Poggendorff's Annalen, that the Prince now believes lithia to be indispensable to the development of grain, he having lately found, that barley did not come to maturity in coarsely powdered and washed rock-crystal, even when supplied with carbonate of lime, magnesia, and manganese, sulphates, phosphates, and fluoride of potassium; but that the addition of nitrate of lithia in the proportion of the 100th of a milligramme, caused it to flower, and to yield perfectly ripe grain.

† See the Gardeners' Chronicle for March 29, 1861.

On this principle, indeed, it is easy to colour the stem of a plant blue, by first immersing its roots in a solution of sulphate of iron, and afterwards in one of ferrocyanide of potassium, when the ferrocyanide of iron will be found wherever the solutions intermix. But no such transmission upwards would seem to take place when an abnormal substance is brought into juxta-position with a living root, until its organisation is destroyed either by mechanical means, or by the poisonous influence of the application itself.

The case, however, is different, when we employ substances normally present in the plant. Here there can be no doubt, that the substances do obtain admission into the system, and that the usual proportions of the respective ingredients may be made to vary, by supplying the roots more plentifully with one ingredient than with the rest.

It has been stated, for instance, by Will and Fresenius, that wheat cultivated near the sea contains more soda and less potassa than it does in more inland situations; and although certain analyses made in my laboratory by Mr. Way, some years ago, would lead to the contrary conclusion, yet in a Memoir read before the Chemical Society in 1853, I brought forward facts which lend support to the view taken by the German chemists, by showing that the relative proportions of potassa and soda present in barley varied, according as the soil was more or less impregnated with one or other of these alkalies.

It will be seen, by reference to the report of these experiments contained in the Chemical Journal, that in this manner the proportion of soda to potassa was made to vary from 23·5 to 15·5 in the grain, and from 27·25 to 20·0 in the straw, thus appearing to show that, to a certain extent, one alkali might replace the other in the vegetable organisation.

But the latest and most extensive series of investigations bearing upon this subject are those by Malaguti and Durocher, recorded in the Annales de Chimie for December, 1858.

The primary object of these chemists was to determine, whether any relation subsisted between the mineral constitution of a plant and its organic structure, as evidenced by the place it occupied as a member of one of the natural families into which the vegetable kingdom is divided.

For this purpose they examined the ashes of 150 plants, selected from twenty-five different natural families, and growing spontaneously in the soil of France, analysing at least three species of each family, in order to estimate the range of variation occurring in them, and distinguishing the arborescent from the herbaceous, as containing a different amount of ligneous fibre.

In the course of these inquiries, two facts were elicited, both of which accord with the results obtained by myself from the experiments above referred to; the first, that plants must possess a power of selection, inasmuch as several species growing on the same soil, abstract from it different amounts of the normal constituents presented to them (see p. 289); the second, that the same species, raised upon different soils, vary to a certain extent in their mineral constitution.

Thus, in argillaceous soils, the proportion of chlorine in the plant is, in general, less than it is in calcareous ones, the range of variation being from 4 to 20 per cent. On the other hand, the amount of sulphuric acid will be greater in argillaceous than in calcareous soils; and the same remark applies, although in a less degree, to the phosphoric acid also.

In like manner, plants grown on calcareous soils contain, in general, more soda and less potassa than in argillaceous ones. Thus, in *Brassica napus* there was present, of soda 5·50, and of potassa 12·34, when grown on a limestone; and of soda 3·00, potassa 25·00 when cultivated upon clay.

Similar differences are pointed out as existing in the case of *Trifolium pratense* and *T. incarnatum*, &c., showing the dependence of the alkaline ingredients upon the chemical constitution of the soil in which these plants were reared.

Liebig, in his Agricultural Chemistry, has pointed out, that in these cases of substitution, the absolute amount of bases present must be exactly equivalent to the acids which the plant contains, or, in other words, that the sum of the oxygen in them is invariable.

Thus, according to Saussure's analysis already referred to, 100 parts of the ashes of a fir from Mount Breven contained—

Carbonate of	potassa .	3·60	in which the O was	0·415
„	Lime .	46·34	„	7·327
„	Magnesia	6·77	„	1·215
			Total of O .	9·007

whilst trees of the same species from Mt. la Salle contained:—

Carbonate of Potassa	7·36	in which the O was	0·850
„ Lime	61·19	„	8·100
„ Magnesia	0·00		——
		Total of O	8·950
		Difference only	0·057
			9·007

And in like manner the ashes of a fir from Allevard, according to Berthier, contained

Of potassa and soda together	16·6	containing of O=	3·57
Lime	29·6	„ „	8·36
Magnesia	3·3	„ „	1·26
			13·10

whilst those of one from Norway contained

Of potassa	14·10	containing of O =	2·40
Soda	20·70	„	5·30
Lime	13·60	„	3·82
Magnesia	4·35	„	1·69
			13·21
		Difference	11
			13·10

These remarkable approximations equally attest the accuracy of the analysts, and the acuteness of the reasoner who first pointed out the relations between the two;—they prove, that the amount of bases is determined by the quantity of acids contained in certain tissues of the plant, and that this amount, however much the nature of the acid may vary, is in each case definite.

But although the quantity of bases present is necessarily dependent upon the amount of acid contained within the plant, it does not follow that even isomorphous bodies, such as potassa and soda, and still less other bases, as lime and magnesia, are capable of replacing each other throughout the entire organism.

The contrary, indeed, would seem, from the following considerations, to be the more probable hypothesis.

In the experiments performed by myself, which have been already noticed, it may be remarked, that the difference in the relative proportions of soda and potassa never rose above 8 per cent.; and yet, if this proportion of soda had taken the place of potassa as a constituent in the organism of a plant, one does not see why the same might not be the case with respect to the whole. On this supposition, the organs of plants would, like the different varieties of augite, garnet, &c., have no definite or fixed composition, the only condition being that their elements should be isomorphous: a position well established with regard to the mineral kingdom, but scarcely applicable, one would think, to the vegetable.

Perhaps the strongest proof that can be adduced in favour of the necessity of a certain fixed chemical constitution for the existence of plants is supplied by the case of those which derive their nourishment from sea water.

If we examine chemically any of the marine algæ, we shall find, that, although containing a considerable proportion of soda, yet, that in many of them, there is present an almost equal amount of potassa. Thus, in the 4th edition of Liebig's Chemistry of Agriculture, 1847, is given the analysis of four species of *fucus*, two of *laminaria*, and twelve of other kinds of algæ. Four of these analyses were made in the laboratory of Giessen; and for the remainder we have the authority of Forchhammer; they present, indeed, many discrepancies, but, upon the whole, concur in establishing, that potassa as often exceeds soda in the constitution of an alga, as the reverse.

I should, indeed, from the difference in the results obtained, be tempted to infer, that a large but variable quantity of sea-water had been circulating through the tissues of the sea-weeds at the times when they were severally collected, and that this had been included in the respective analyses. At any rate, if soda were capable of replacing potassa in the system of a plant, one does not see, why any potassa at all, except an infinitesimal quantity, should be present in them, considering that sea water, which alone can supply the mineral constituents present in the organisation of a marine plant, contains an infinitely smaller amount of potassa than it does of soda.

The case might have been put even more strongly, if I had adverted to the quantity of iodine which sea plants extract from the waters of the ocean, although the proportion of that ingredient, which is known to exist in the latter, can, from its minuteness, be hardly detected, even by the most delicate tests.

Hence iodine, as it would seem, can no more be replaced by chlorine in the organism of marine plants, than potassa can by soda, although both the one and the other are regarded as isomorphous.

Liebig, in his Letters on Modern Agriculture (page 44), has illustrated this principle by the case of the common duckweed of our ponds, the *Lemna trisulca*, growing in a bog, the water of which contained the following salts, in such proportions, compared with those present in the plant, as indicated a power of selection residing in the latter.

Thus there were present in seventy-six parts:—

	of the soil	of the duckweed.
Lime	35·000	16·820
Magnesia	12·264	5·080
Chloride of sodium . . .	10·100	5·897
Potassa	3·970	13·160
Soda	0·471	..
Oxide of iron and traces of alumina	0·721	7·360
Phosphoric acid	2·619	8·730
Sulphuric acid	8·271	6·090
Silica	3·240	12·250
Chloride of potassium	. .	1·450
Total	76·656	76·837

We must here admit a certain power of selection residing in the roots of the plant, since, whilst the water contained in 76 parts, of lime about 35, and of magnesia 12 per cent., the plant had abstracted only 16·8 of the former, and 5 of the latter element; and whereas the proportion of potassa in the water was less than 4, that in the plant was 13; of phosphoric acid in the water 2·6, in the plant 8·7; of silica in the water 3·2, in the plant 12·2.

But, in fact, we need not go so far for proofs of this familiar principle; for, as every plant possesses a different chemical constitution, it is evident that of several species grown in the same soil, each one must exercise a kind of selection, in order to extract from the same material the several ingredients which it requires for its separate organisation.

I have already* attempted to reconcile the apparent discrepancy between the above two classes of phenomena,—namely, the variations in the composition of a plant which may be induced by artificial means, and the necessity for the presence of certain specific mineral ingredients in their organisation, by supposing that the proximate principles existing in a vegetable are fixed and invariable, a seed possessing a certain percentage of phosphoric acid which cannot be replaced by any other ingredient, a mass of ligneous fibre a certain amount of potassa, &c.; but that, independently of the acids and bases which enter into their composition, and make up the fabric of the plant, there is always circulating through its tissues a certain amount of alkali, one function of which, according to Liebig, is to promote the fixation of carbonic acid; and that, as the latter duty may be discharged by one alkali as well as by another, it is conceivable, that potassa and soda, or even lime and magnesia, may replace one another, so far as respects the fluids which are circulating through the vegetable tissues.

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* See vol. v. of this Journal, 1853.

Hence we may understand, how it is, that one portion of the alkaline or other mineral ingredients, present in a plant, may be definite as to quality, whilst another portion may vary according to circumstances; and accordingly, whilst it is found that each proximate principle presents a fixed chemical composition, the entire plant may, nevertheless, vary within certain limits, as it will contain an uncertain amount of unassimilated sap flowing through its system at the time when it was cut down.

There is also another cause for the different composition of the ashes of the same species of plant, namely, a variation in the ratio subsisting between the proximate principles themselves. Thus, one particular climate, or mode of culture, may favour the production of gluten, another that of starch; and thus the seed of the same plant, in different localities, may not always be identical in point of composition. Thus, I have given instances, in my "Lectures on Agriculture," published in 1841, in which the application of nitrate of soda to a soil added 4·25 to the amount of gluten present in the crop of wheat growing in it; and Davy affirms that the flour of warm climates contains, in general, more gluten than that of colder ones.*

Upon the whole, then, I should be inclined to infer, that the spongioles of the roots have residing in them some specific power of excluding those constituents of the soil which are abnormal, and, therefore, unsuitable to the plant, but that they take up those which are normal in any proportions in which they may chance to present themselves; the redundant portion, however, left after the necessities of the organism have been provided for, being again excreted, so that a vegetable will only vary in mineral composition in proportion to the relative amount of the several proximate principles which may be produced under the peculiar circumstances of its cultivation, or of the climate it enjoys.

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* See also Boussingault, Ann. Ch. Phys. [2], lxv, 301.

If it be questioned, whether we can concede to the absorbing surfaces of the roots a function so nearly allied, in semblance at least, to volition, I would refer to the observations of Huxtable and Thomson, and more especially to the valuable Memoirs of Way, as establishing the existence of a property connected with these organs of no less extraordinary a nature; namely, that whilst the carbonate of ammonia, present in rain-water and in manures, is so firmly fixed in the soil, that, under ordinary circumstances, water containing carbonic acid seems unable to withdraw it, the same is nevertheless commonly absorbed and conveyed into the tissue of plants by means of their roots.

Hence, as Liebig observes, vegetables must obtain their nourishment by virtue of some specific attraction exerted by the rootlets upon the ingredients locked up within the earth; a property, wonderful, indeed, but not more so, than that possessed by the leaves, of converting carbonic acid into other organic principles by the elimination of oxygen.

In a Paper published in the Philosophical Transactions for 1836, "On the Action of Light upon Plants, and of Plants upon the Atmosphere," I concluded, that light operates upon the vegetable, as it does upon the animal kingdom, in the character of a specific stimulus, so that the formation of the various secretions elaborated from the carbonic acid absorbed, is not a purely chemical process, but is due to some peculiar agency of the green parts connected with, and dependent upon, their vitality.

I would now extend the same inference to the roots, considering that, when in a healthy and vigorous condition, they serve as instruments for conveying to the other parts of a plant those juices, which contain substances calculated for affording them nourishment, and for excluding others which might be useless or injurious to them.

Liebig, indeed, goes so far as to contend, that the mineral matters presented to the spongioles are not in a soluble form; for if they were, he suggests, that water, either alone or in conjunction with carbonic acid, would be capable of abstracting them from the earth. He therefore imagines, that, being distributed over the general body of the soil in a finely divided condition, they are taken up by the rootlets, owing to a kind of specific attraction. We can thus more readily understand, how it is that certain ingredients are absorbed in larger quantities than others, and why some even should be absolutely rejected, as in the case of the common duckweed, to which Liebig refers.

It is remarkable that, although alumina is not usually present in the ashes of plants, yet that one tribe, namely, the *Lycopodiaceæ*, contains it in large quantities,*—a fact which I have myself verified.

By what precise agency this usually insoluble earth† finds its way into the vegetable economy seems to be yet undetermined; but its occurrence in a few plants may be regarded as a proof that it would have been taken up in all, if the spongioles were merely passive instruments for absorbing and transmitting indiscriminately whatever was presented to their external surfaces.

But, indeed, the whole efficacy of geothermal culture, now so much insisted on by horticulturists, seems to pre-suppose, that the roots are vital agents, capable of being acted upon by stimuli. Why else should the application of heat to the roots impart greater vigour to the upper parts of a tree, and cause, as in the case of the *Bougainvillea*, the copious development of flowers where none before were produced; and, on the other hand, why, as happened in so many cases during the late severe winter, should the plant be destroyed in consequence of the cold penetrating into the ground, whilst it resisted the influence of the frost so long as its roots were protected?

If the spongioles acted upon the surrounding matter simply by virtue of endosmose, as a dead membrane might do, the process of absorption, although it might be arrested by frost, would be renewed when the mild weather returned, and the plant would sustain no further damage than what might be due to a temporary suspension of its functions; whereas the consequence of the late extreme cold appears to have been, that the roots became unfitted for discharging their office, and that the stem and branches suffered, not only negatively, by the deprivation of proper nourishment, but positively, by receiving noxious matter from the ground. In short, the spongioles may be supposed to have been reduced to the same condition by the cold, as that to which they would be brought by the application of a poisonous solution, such as the sulphate of copper already alluded to; and in both cases the same consequences would ensue.

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* *L. chamæcyparissus*, 39·07; *L. clavatum*, 20·69; according to Ratthausen, in Liebig's "Jahresbericht" for 1853, p. 586.

† The late researches of the Master of the Mint, which were not known to me at the time of the reading of this Paper, show that alumina is capable of existing in a soluble condition combined with water.

Let us now consider, how the influence of poisons upon the vegetable economy is to be reconciled with the principles just laid down.

It is notorious, that a moderate dose of certain mineral as well as of vegetable poisons applied to the roots of a growing plant destroys its vitality, as certainly and as speedily, as if the same were injected into any part of the stem or branches. It is, therefore, evident, that the poison does not merely exert a *local* influence upon the part to which it is applied, but that it must be absorbed and transmitted through the other parts of the organism. But how, it may be asked, is this fact to be reconciled with the power of rejecting such abnormal ingredients as are presented, which we have ascribed to the roots?* The reason I conceive to be, that the deleterious quality of the substance destroys the vitality of the part, and thus reduces it to the condition of a simple membrane, which by endosmose absorbs whatever is presented to its external surfaces.

The same thing may be supposed to happen generally in the case of poisons of a certain degree of intensity, as in that of the solution of sulphate of copper, which Saussure and others have fully ascertained to be taken up in larger quantity than any other soluble material. In all such instances, however, the absorption of the poison was speedily followed by the death of the plant.

When, on the contrary, the poison is presented in a more diluted form, the effect resulting would seem to be a matter of rather greater uncertainty, as the statements made on the subject are of a conflicting nature. On the one hand, Dr. Edmund Davy, Professor of Agriculture and Agricultural Chemistry in the Dublin Society, is quoted in the Gardener's Chronicle for September 10th, 1859, as having ascertained, that peas watered with a saturated solution of arsenious acid for more than a week continued to the last uninjured, although arsenic was readily detected by appropriate tests in the plants subjected to this treatment. He is also reported to have stated, that a solution of superphosphate of lime, which, if impure sulphuric acid has been employed in its preparation, always contains more or less arsenic, was applied to a cabbage plant, which nevertheless grew and flourished, although arsenic was detected in it afterwards. A similar experiment was tried also upon turnips with the same results. Mr. Horsley, of Cheltenham, has since published a letter addressed to Dr. Edmund Davy, in which he confidently affirms the same fact, and assures us that it holds good in the case of all the various plants upon which he had experimented.

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* One of the few cases recorded, on competent authority, in which an abnormal substance appears to be taken up by a plant, without, apparently, affecting its healthy condition, is that of the violet which grows on the calamine rocks near Aix la Chapelle, and is found to contain zinc amongst its mineral constituents.—See Annals of Natural History, vol. xiv, second series, for 1854.

On the other hand, Jäger, Humboldt, and Link could not induce plants to grow when sprinkled with arsenicated water, and Mr. Ogsden (in the Gardener's Chronicle for March 10th, 1860,) states, that on repeating Davy's experiments, he found cabbage plants, and also Scotch kale, to droop and die within a week after the application of the arsenical solution. In neither of these cases was any arsenic detected in the leaves, or higher up in the stem, than about 5 inches from the ground.

In corroboration of these results, it might be unfair to add those arrived at by Marcet, as he plunged the shoot of a kidney-bean, and not its roots, into the arsenical solution made use of, which contained, it seems, 2 grains of arsenious acid in 2 ounces of water. Under such circumstances, the death of the plant which ensued cannot well be cited as an argument from analogy as to what might happen in the case of the spongioles of the roots; but the immunity which the potatoe crop in the neighbourhood of Swansea seems to enjoy from the influence of the arsenical fumes with which the atmosphere thereabouts is so infected, and likewise the fact, that, in certain parts of Cornwall, where arsenical pyrites from the mines is thrown upon the soil in large quantities, the crops do not appear to suffer, and contract, in consequence, no injurious properties, may perhaps be fairly adduced in support of this same conclusion.

I will now lay before the Society a few experiments bearing upon the same subject which have been carried on by myself.

I possess, in the first place, some notes of an experiment made so long ago as 1837, in which plants were watered with a solution of arsenious acid in the proportion of 1 grain of the mineral to 3 pints of water, and where no trace of arsenic could be detected in them after the application.

Passing over these trials, which appear wanting in the requisite precision, I will state what I have done during the past year, with a view of determining the power of the roots to absorb poisons and abnormal substances, when presented to them in a state of great dilution.

Having first made a few tentative experiments on a small scale, with the view of ascertaining what amount of arsenious acid might be applied to a growing plant with impunity, I watered a plot of ground, 25 feet long by 4 feet wide, containing a crop of young barley, with a solution of arsenious acid, in the proportion of 2 ounces to 10 gallons of water. Finding, six days afterwards, that the barley appeared to be blighted, I applied to a second plot, of the same dimensions, a solution of just half the strength of the preceding, containing 1 ounce of arsenious acid to 10 gallons of water.

After two applications, with an interval of twelve days between, viz., on July 16th and 28th, this crop also appeared to be somewhat damaged; but nevertheless the application was renewed on August 11th, 18th, and 21st, so that, on the whole, the solution was applied five times without preventing the crop from arriving at maturity.

A similar plot of ground, sown with turnips, was watered on the 3rd, 10th, 17th, and 27th of September, with a solution containing 1 ounce of acid to 10 gallons of water; so that, on the whole, 4 ounces of arsenious acid diluted with 40 gallons of water had been added.

Upon the turnips no sensible effect was produced by the application, the bulbs appearing as large, and the tops as luxuriant as they were in the rest of the bed which had not been so treated.

It may be worth remarking, although perhaps the circumstance might be owing to other causes, that the barley so watered arrived at maturity a fortnight earlier than the rest of the crop.

The produce was somewhat less than the average in the other parts of the field, which in every 100 square feet was found to yield 12lbs. of straw, and 4lbs. 14 oz. of grain; the produce in the portion treated with arsenic being 10½ lbs. of straw, and 3½ lbs. of grain. The weight of the latter to the bushel was 52 lbs., whereas, that of the other portion was only 50 lbs.

The turnips from the arsenicated portion when arrived at maturity, yielded of

Roots	..	..	51 lbs
Tops..	..	..	20 „

whilst a similar portion of the same bed not treated with arsenic yielded

Of roots	..	..	58 lbs.
Tops	..	..	22 „

Thus much with respect to the influence of the poison upon the amount and quality of the production.

With the view of ascertaining whether these crops had really taken into their system any appreciable quantity of arsenic, the following method was adopted.

1st. With respect to the barley.

A portion of the grain was burnt in an earthen crucible, with plenty of nitrate of potassa, and the ashes were treated with hydrochloric acid. Sulphuretted hydrogen was then passed through the solution, but no precipitate was occasioned by its addition.

As however, it might be suspected that the arsenic had been driven off by the heat, notwithstanding the presence of nitre, by which it was intended to fix it, a second portion of the grain was heated in a glass retort for 5 hours together, with some nitro-hydrochloric acid. The liquor was maintained at a boiling temperature, and the vapour that came over, collected and tested with sulphuretted hydrogen as before.

In this instance, a slight precipitate was obtained, which afforded indications of arsenic by Marsh's test.

As however it was possible that a trace of this substance might have adhered to the external surface of the husk, from its having been sprinkled with the solution, a second portion of the barley was carefully washed before subjecting it to the same treatment, and here the indications were much less decisive, a very slight stain being perceived upon the subliming tube, but one of a reddish colour, and less distinctly arsenical in its appearance than the former.

The suspicion thus created, as to the presence of arsenic in the case of the barley being merely superficial, was confirmed by my examination of the turnips, which had been similarly treated with an arsenical solution; for here the root, after being sliced into thin pieces and dried, was treated with a solution of chlorate of potassa, according to the plan recommended by Wöhler*, and the liquor, after filtration, subjected to the action of sulphuretted hydrogen. Here, as a dirty, greyish precipitate was thrown down, I might have suspected the presence of arsenic, but this presumption was overturned by the application of Marsh's test, which afforded no indications of arsenic whatever. I may also add, that Professor Brodie was good enough to submit another sample of the same turnips to chemical examination in his laboratory, but was unable to detect the presence of arsenic in it.

I also, on the 10th of last July, applied to a plot of similar dimensions with the former, containing a crop of barley, a solution of 4 ounces of nitrate of baryta in 4 gallons of water. The application was repeated on the 18th and 28th of July, and on the 11th, 18th, and 21st of August. No perceptible effect was produced upon the crop so treated, although the amount of grain was reduced from 4½lbs. in the 100 square feet, to 3¼ lbs. This, however, might be an accidental difference: for after a similar application to a crop of turnips, the weight of the roots somewhat exceeded the average of the crop in the rest of the same plot, weighing in 100 square feet 62 lbs., whilst the average of the remainder was 58 lbs.

Here the solution of nitrate of baryta was applied on September 3rd, 10th, 17th, and 27th, without any perceptible influence upon the character of the crop.

At the same time, similar experiments were made upon two corresponding crops of barley and turnips, by the application to them of 10 ounces of nitrate of strontia in 10 gallons of water, the application being renewed five successive times. No perceptible difference in either case resulted from the application in the character of the crop, and its amount in either instance seemed enhanced, but this might perhaps have been owing to other causes.—The following were the results obtained :—

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* Hand-book, p. 218.

			In 100 square feet treated with strontian.		In 100 square feet not so treated.
Barley ..	Grain	..	5 lb.	..	4½ lb.
	Straw	..	16 ,,	..	11 ,,
Turnips ..	Roots	..	53 ,,	..	40 ,,
	Tops	..	13 ,,	..	20 ,.

The barley and barley-straw, the turnip roots and tops, which had been watered with the above two solutions, were separately incinerated, their ashes reduced to whiteness by heat, then treated with nitric acid, and the solution evaporated to dryness and exposed to a red heat. They were then severally dissolved in hydrochloric acid and filtered. To the filtered solution sulphate of soda was added, and the precipitate formed was washed and dried.

Presuming the latter to consist of the earthy sulphates, I exposed each of them to a red heat for half an hour, mixed with an equal weight of carbonate of soda. The mass was then digested in water, and to the undissolved residue, muriatic acid was added.

So far the process was the same in all the eight cases; but to the hydrochloric acid solution, derived from the plants that had been watered with nitrate of baryta, after driving off the water, alcohol of specific gravity of ·810 was added. The salt derived from the grain of the barley was wholly dissolved by the alcohol: and was, therefore, inferred to consist entirely of chloride of calcium. That from the barley straw, as well as those from the turnip tops and roots, left, it is true, a slight residuum insoluble in the alcohol; but in only one of them, namely, that derived from the turnip tops, did the residuum, when dissolved in water, yield any precipitate with sulphate of soda; and, therefore, in that alone was the presence of baryta established.

Here then we are drawn to the same conclusion as in the case of the arsenic, namely, that the earth was not taken into the system of the plant, but had merely adhered to its external surfaces.

With regard to the other five solutions, which were derived from the ashes of plants watered with a solution of nitrate of strontia, after dissolving them in hydrochloric acid, and evaporating to dryness the solution obtained, they were severally treated with absolute alcohol like the former.

As, however, this menstruum takes up chloride of strontium as well as chloride of calcium, I trusted for the detection of the former earth to two tests, namely, first—the colour of the flame produced by setting fire to the alcoholic solution; and secondly—the effect of the addition to it of a weak solution of sulphate of soda. Now, in neither of these ways could I obtain any indication of the presence of strontia in the salt derived from the grain of the barley or from the roots of the turnips; but a slight precipitate was produced by the addition of sulphate of soda in the case of the barley straw and of the turnip tops, referable, as I conceive, to the same cause as the presence of baryta and arsenic in the foregoing cases, namely, to the adherence of a small quantity of the earthy salt to the external surfaces of the plant to which the solution had been applied.

I have trespassed upon the time of the Society in the detail of these experiments to a greater extent than I should have been otherwise disposed to do, out of consideration for those chemists who have arrived at conclusions opposite to my own; as it seemed but right to give to others ample means of judging, how far my experiments are calculated to shake their confidence in the results previously obtained.

The facts indeed which I have brought forward in this Memoir are, I must admit, too few in number, and, perhaps, too deficient in the required precision, to settle the question at issue; and I have consequently this very year commenced a similar set of experiments, in which I hope to have avoided the source of possible error which has been pointed out in those already undertaken,—namely, the adherence of some portion of the salt applied to the external surfaces of the stem and leaves of the plant, by introducing the salt into the soil before the seed is sown. I have also substituted the arsenic acid for the arsenious, conceiving that, being isomorphous with phosphoric acid, it has a better chance of being assimilated.

Whilst, however, I abstain from expressing a decided judgment as to the question at issue, I cannot help entertaining a confident belief, that as the results to which my experiments appear to point, seem more in accordance with the general principles of vegetable physiology than those opposed to them, further investigations will establish the fact, that whenever abnormal substances are taken up by a living plant, it is in consequence of some interference with the vital functions of the roots, caused, in the first instance, by the deleterious influence of the agent employed.*

XIX. *On Colouring Matters derived from Coal Tar.*

By W. H. Perkin, Esq.

The subject of the present communication is one which is remarkable for the very rapid progress it is making. Previous to the year 1856, the colouring matters derived from "Coal Tar products" were practically unknown; but, owing to recent discoveries, they now rank amongst the most important colouring matters employed. Only a few of them, however, are actually used by the dyer and printer; the rest have merely a scientific interest, and for reasons presently to be mentioned, are not likely to acquire any other.

The coal-tar products which have up to the present yielded colouring matters are numerous. The following is a list of the most important, which are obtained either directly or indirectly from coal-tar:—

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* In stating this as my belief, I do not pretend to pronounce what substances are to be regarded as abnormal either to vegetables in general, or to certain species in particular.

The late investigations, carried on by means of the spectrum, have shown, that even lithia is normally present in the ashes of tobacco; and, from the experiment of the Prince of Salm Horstmar, alluded to in p. 214, it might be conjectured that this alkali was present in plants generally.

Copper also was detected in them, as early as 1816, by Dr. Mupner (see Scwheigger's Journal), and by Sarzeau, in eleven different kinds, in 1830. (Journal de Pharmacie.) These latter statements, indeed, have been called in question by Danger and Flandin; but they appear to be substantiated by the later researches of Dr. Odling, recorded in the "Guy's Hospital Reports, 1858."

The latter found copper in flour, in grain, in the straw of wheat and barley, in mangel-wurzel, and in Swedish turnips, as well as in a variety of animal substances. But the quantity discovered in these instances was so minute as to lend no countenance to the idea, that so large an amount of sulphate of copper as that taken up by plants in the cases reported by Saussure, could have found its way into their organism, if the vitality of the roots had continued unimpaired.

Aniline and its Homologues,
Carbolic acid,
Chinoline or Quinoline,
Naphthaline, and
Pyrrole bases.

1. *Aniline.*

ANILINE was discovered in 1826 by Unverdorben. The original method employed for its preparation was by digesting indigo with hydrate of potassium, and subjecting the resulting product to distillation. Aniline was also obtained from the basic oils of coal-tar. But the process which is now employed for its preparation is a remarkable instance of the manner in which abstract scientific research becomes in the course of time of the most important practical service.

Benzole was discovered by Faraday, who obtained it from oil gas. After this, it was produced by distilling benzoic acid with baryta, which result determined its formula, and was the cause of its being called benzole. After this, Mansfield found it to exist very abundantly in common coal-tar naphtha, which is the source from which it is now obtained in very large quantities.

Benzole, when studied in the laboratory, was found to yield, under the influence of nitric acid, nitrobenzole. Zinin afterwards discovered the remarkable reaction which sulphide of ammonium exerts upon nitrobenzole, converting it into aniline; and, lastly, Béchamp found that nitrobenzole was converted into aniline when submitted to the action of ferrous acetate. It is Béchamp's process which is now employed for the preparation of aniline by the *ton.* Had it not have been for the investigations briefly cited above, the beautiful aniline colours, now so extensively employed, would still be unknown.

When I discovered aniline purple, nitrobenzole and aniline were only to be met with in the laboratory. In fact, half a pound of aniline was then esteemed quite a treasure; and it was not until a great deal of time and money had been expended, that I succeeded in obtaining these substances in large quantities, and at a price sufficiently low for commercial purposes.

The colouring matters obtainable from aniline are numerous. They are the following:—

Aniline Purple.
Violine.
Rosine.
Fuschine.
Alpha-aniline Purple.
Bleu de Paris.
Nitrazophenyline.
Dinitraniline.
and Nitrophenylene-diamine.

ANILINE PURPLE.

Generally known as Tyrian Purple, Mauve dye, Phenamine, Indisine, &c.

It has been known for many years that the hypochlorites react on aniline and its salts, producing a purple solution. In fact, hypochlorites are the distinguishing test for aniline; but nothing definite was known of the nature of this purple solution, it being simply stated that aniline produced with hypochlorites a purple liquid, but that its colour was very fugitive.

As many very absurd statements have been made respecting the discovery of aniline purple, I will just briefly mention how it was that I first became acquainted with it.

In the early part of 1856, I commenced an investigation on the artificial formation of quinine. To obtain this base, I proposed to act on toluidine with iodide of allyl, so as to form allyl-toluidine, which has the formula:—

$$\left.\begin{matrix}C_7H_7\\C_3H_5\\H\end{matrix}\right\} = C_{10}H_{13}N,$$

thinking it not improbable that by oxidising this, I might obtain the desired result, thus:—

$$\underset{\text{Allyl-toluidine.}}{\underline{2(C_{10}H_{13}N)}} + O_3 = \underset{\text{Quinine.}}{\underline{C_{20}H_{24}N_2O_2}} + H_2O$$

For this purpose, I mixed the neutral sulphate of allyl-toluidine with bichromate of potassium; but, instead of quinine, I obtained a dirty reddish brown precipitate. Nevertheless, being anxious to know more about this curious reaction, I proceeded to examine a more simple base under the same circumstances. For this purpose I selected aniline, and treated its sulphate with bichromate of potassium. This mixture produced nothing but a very unpromising black precipitate; but, on investigating this precipitate, I found it to contain that substance which is now, I may say, a commercial necessity, namely, *aniline purple.*

The method adopted for the preparation of aniline purple is as follows:—Solutions of equivalent proportions of sulphate of aniline and bichromate of potassium are mixed and allowed to stand till the reaction is complete. The resulting black precipitate is then thrown on a filter and washed with water, until free from sulphate of potassium. It is then dried. This dried product is afterwards digested several times with coal-tar naphtha until all resinous matter is separated, and the naphtha is no longer coloured brown. After this it is repeatedly boiled with alcohol to extract the colouring matter. This alcoholic solution when distilled leaves the colouring matter at the bottom of the retort, as a beautiful bronze-coloured substance.

Before speaking further of the colouring matter, I will just describe the secondary, or, more properly, the primary products of the action of bichromate of potassium on sulphate of aniline, as nearly nine-tenths of the aniline employed in the preparation of aniline purple are converted into these useless substances.

These products are two in number, namely, the resinous matter which is separated from the black precipitate by means of coal-tar naphtha, and the residue which is left after the colouring matter has been extracted. The resinous matter, when separated from the coal-tar naphtha, consists of a brownish black pitch, which is fusible when heated. It is soluble in alcohol, ether, turpentine, bisulphide of carbon, and many similar solvents. It possesses one remarkable property, viz., that when its solutions in hydrocarbons are acidified with strong acids and well agitated, all the resinous matter is thrown out of solution and precipitated. Alkalies render it soluble again. These facts would make it appear to be a weak organic base.

This substance contains about 10 per cent. of nitrogen. It dissolves in fuming nitric acid, and by ebullition yields a yellowish brown acid. Anhydrous bichloride of tin, when heated with it, does not yield any colouring matter.

The residue which is left after the colouring matter has been separated is a purplish black powder. It contains about 30 p.c. of oxide of chromium. It is insoluble in all solvents, with the exception of strong acids, and is remarkable for the readiness with which it takes fire. It has been used for the manufacture of black paint and printer's ink. As it contains large quantities of carbon and oxide of chromium, it would form a most valuable product for the preparation of anhydrous chloride of chromium.

The aniline purple prepared according to the process just described, although suitable for practical purposes, is not chemically pure. If required pure, it is best to boil it in a large quantity of water, then filter the resulting coloured solution, and precipitate the colouring matter from it by means of an alkali. The precipitate thus obtained should be collected upon a filter, washed with water until free from alkali, and dried. When dry it is to be dissolved in absolute alcohol, the resulting solution filtered, and then evaporated to dryness over the water bath.

Thus obtained, aniline purple appears as a brittle substance having a beautiful bronze-coloured surface; but if some of its alcoholic solution be evaporated on a glass plate, and viewed by transmitted light, it appears of a beautiful bluish violet colour. If considerable quantities of an alcoholic solution of the colouring matter containing a little water be evaporated to dryness, the surface of the colouring matter next to the evaporating dish, often exhibits a golden green appearance when detached.

Aniline purple is difficultly soluble in cold water, although it imparts a deep purple colour to that liquid: it is more soluble in hot water; but its hot aqueous solution, when left to cool, assumes the form of a purple jelly. It is very soluble in alcohols, though nearly insoluble in ether and hydrocarbons. Aniline dissolves it readily. In properties it seems to be slightly basic, as it is more soluble in acidulated than in pure water. Alkalies and saline substances precipitate it from its aqueous solutions as a dark purplish black powder. Bichloride of mercury precipitates it in a very finely divided state. A little of this precipitate (which appears to be a double compound of chloride of mercury and colouring matter) when suspended in water, and viewed by transmitted light, appears of a blue or violet colour.

A small quantity of hydrate of potassium or sodium added to an alcoholic solution of the colouring matter causes it to assume a violet tint, but without effecting any change in the colouring matter itself. Ebullition with alcoholic potash does not decompose it.

Aniline purple dissolves in concentrated sulphuric acid, forming a dirty green solution which, when slightly diluted, assumes a beautiful blue colour; excess of water restores it to its original purple colour. It may even be heated for an hour to 100°C. with Nordhausen sulphuric acid without suffering decomposition, being restored to its original colour by means of water, and possessing precisely the same properties it had before being subjected to this powerful agent. Hydrochloric acid acts upon it in the same manner as sulphuric acid. It is decomposed by chlorine, and also by fuming nitric acid. Bichloride of tin is without action upon it.

Powerful reducing agents have a peculiar action upon this colouring matter, somewhat analogous to the action of reducing agents on indigo. An alcoholic solution of sulphide of ammonium mixed with an alcoholic solution of aniline purple, causes it to assume a pale, brownish tint. This solution, when brought in contact with the atmosphere, instantly recovers its original beauty and intensity of colour. An alcoholic solution of the colouring matter mixed with a little protoxide of iron, changes to a pale brown colour. This solution also becomes purple when exposed to the action of the atmosphere; sulphurous acid does not affect the colour of this substance.

Aniline purple forms a remarkable compound with tannin. When an aqueous solution of it is mixed with a solution of tannin, precipitation takes place. The precipitate thus formed after having been well washed, no longer possesses the properties of the pure colouring matter. It is insoluble in water. Like the pure aniline purple, it dissolves in concentrated sulphuric acid, forming a dirty green liquid; but on adding an excess of water to this solution, the new compound is precipitated unchanged; this compound is rather duller in colour than the pure colouring matter itself.

Aniline purple, when agitated with a little moist binoxide of lead, is transformed into *rosine*. It is remarkable for its intensity of colour, a few grains of it colouring a considerable quantity of spirits of wine.

VIOLINE.—This colouring matter, which is a product of the oxidation of aniline, was first obtained by Dr. D. Price, who prepares it by heating an aqueous liquid containing two equivalents of sulphuric acid, and 1 eq. of aniline to the boiling point, and then adding 1 eq. of binoxide of lead, boiling the mixture for some time, and filtering it while hot. The filtrate, which is of a dark purple hue, is boiled with potash, both to separate the excess of aniline, and also to precipitate the colouring matter; when all the free aniline has volatilized, the residue is thrown on a filter and slightly washed with water, and then dissolved in a dilute solution of tartaric acid. This solution, after filtration, is evaporated to a small bulk, re-filtered, and then precipitated by means of an alkali.

Thus obtained, violine presents itself as a blackish purple powder, which when dissolved in alcohol and evaporated to dryness, appears as a brittle bronze-coloured substance, similar to aniline purple, but possessing a more copper-coloured reflection. It is even less soluble in water than aniline purple. It is very soluble in alcohol, but insoluble in ether and hydrocarbons. Its solutions possess a colour somewhat similar to that of the field violet. Concentrated sulphuric acid dissolves it, forming a green solution, but excess of water restores it to its original colour.

The colour of violine, like that of aniline purple, is destroyed by reducing agents, but restored by the action of the atmosphere. Tannin produces an insoluble compound with it. When agitated with a small quantity of binoxide of lead, it is converted into aniline purple; excess of this re-agent changes it into roseine.

ROSEINE.—This substance almost always accompanies aniline purple, though in very small quantities. It was first noticed publicly by C. Greville Williams, and afterwards by Dr. D. Price. Williams used manganates for its preparation, but Dr. D. Price prepared it by means of binoxide of lead; his process is as follows. To a boiling solution of 1 equivalent of sulphate of aniline, 2 equivalents of binoxide of lead are added, and the mixture is boiled for a short time. The rose-coloured solution is then filtered, and the filtrate evaporated to a small bulk, which causes a certain amount of resinous matter to separate. This evaporated solution is then filtered, and the colouring matter precipitated by means of an alkali; it is then collected on a filter, slightly washed, and then dried. The colouring matter thus prepared readily dissolves in alcohol, forming a fine crimson-coloured liquid which, when evaporated to dryness, leaves the colouring matter as a dark brittle substance, having a slightly metallic reflection. It is much more soluble in water than either aniline purple or violine, but like them, it is insoluble in hydrocarbons, and more soluble in acid than in neutral liquids. Concentrated sulphuric acid dissolves it, forming a green solution;

excess of water restores it to its original colour. It forms a compound with tannin, and is also decolorized, or nearly so, by powerful reducing agents.

The three colouring matters just mentioned, viz., aniline purple, violine, and roseine, are evidently closely allied, for they have nearly the same properties. They are all formed under similar circumstances, namely, by the action of oxidizing agents in the presence of water. They are all slightly soluble in water, though, as the shade of colour becomes redder, so does their solubility increase. Alkalies precipitate them from their aqueous solutions. Concentrated sulphuric acid dissolves them all, forming green solutions, which excess of water restores to the original colour of the colouring matter; powerful reducing agents deprive them of their colour, (or nearly so), but it is restored by the influence of oxygen; and lastly, tannin forms insoluble compounds with them all.

Fuchsine or Magenta.—This beautiful product, which is often improperly called roseine, is a member of an entirely different series of compounds to the foregoing, being formed under very different circumstances, and possessing very different properties. It was first observed by Natanson, in 1856, when studying the action of chloride of ethylene on aniline, and afterwards (shortly before it was practically introduced into the arts), by Dr. Hofmann, when preparing cyantriphenyl-diamine by the action of bichloride of carbon on aniline. It was M. Verguin who first brought it forward as a dyeing agent, and who, I believe, taught manufacturers how to prepare it on the large scale.

Fuchsine is invariably formed at a temperature ranging from 170° to 190°C. It is produced from aniline, by the action of reducible chlorinized, brominized, iodized, or fluorized substances, as well as by weak oxidizing agents. The substances generally used for its preparation on the large scale, are the perchlorides of tin and of mercury, and the nitrates of mercury.

Preparation of Fuchsine by the action of Bichloride of Tin on Aniline.—Aniline combines with bichloride of tin, evidently producing a double compound; this product is a whitish substance, and may be prepared by adding to aniline bichloride of tin in the anhydrous state, or dissolved in water. Anhydrous bichloride of tin combines with aniline with great energy to form this compound.

To prepare fuchsine from the double compound, it is necessary that it should be free from water, or nearly so: hence anhydrous bichloride of tin is generally employed for its preparation. The process adopted is as follows.—Anhydrous bichloride of tin is slowly added to an excess of aniline, the mixture being constantly stirred, and the pasty mass thus formed gradually heated. As the temperature increases, it becomes quite liquid, and also brown in colour. As soon as the temperature nearly approaches the boiling point of the mixture, it rapidly changes to a black-looking liquid, which, when viewed in thin layers, presents a rich crimson colour. This is kept at its boiling point some time, and then well boiled with a large quantity of water; by this means, the principal part of the colouring matter is extracted, together with considerable quantities of hydrochlorate of aniline. The residue is a solid, of a brown colour, and contains considerable quantities of tin in the form of a proto-compound.

The aqueous solution of the colouring matter and hydrochlorate of aniline is then boiled, so as to volatilize any free aniline it may contain, and then saturated with chloride of sodium. The chloride of sodium causes the colouring matter to separate as a semi-solid pitchy substance, of a golden-green aspect, while the hydrochlorate of aniline remains in solution. The colouring matter thus obtained may be further purified by digestion with benzole, which dissolves out a certain amount of resinous matter.

Preparation of Fuchsine by the action of Mercurous Nitrate on Aniline.—When mercurous nitrate is left in contact with aniline for some time, it forms a white pasty mass, but when carefully heated to 170°C. or 180°C., it reacts upon it, forming a brown liquid, which gradually changes to a dark crimson; at the same time the whole of the metal of the mercury-salt collects at the bottom of the vessel. This product, when separated from the metallic mercury, and allowed to cool, becomes semi-solid, being filled with crystals of nitrate of aniline.

To purify this product, it is best to dissolve out the nitrate of aniline it contains in a small quantity of cold water, and then to boil the remaining product several times with fresh quantities of water, until the principal portion of the colouring is extracted, and filtering the resulting aqueous solutions while hot. On cooling, these solutions deposit the colouring matter as a golden green tarry substance, from which benzole separates a small quantity of a brown impurity, leaving the colouring matter as a brittle solid.

I have briefly described the above processes, because they may, to some extent, be regarded as types of most of the methods employed for the production of this colouring matter, the first representing its formation by the action of reducible chlorides upon aniline, and the latter, by the influence of weak oxidizing agents upon aniline.

Fuchsine is undoubtedly an organic base, and a more powerful one than is generally supposed. The product obtained from aniline by means of bichloride of tin, is the hydrochlorate of fuchsine, and that obtained by the oxidizing action of nitrate of mercury is the nitrate of fuchsine.

Fuchsine is separated from its salts by precipitation with a small quantity of ammonia.

When freshly precipitated, it is a red, bulky paste, which, on drying, contracts to a purplish red powder. It is but sparingly soluble in water, though moderately soluble in alcohol; it is insoluble in ether and hydrocarbons. A small quantity of hydrochloric acid causes it to dissolve freely in hot water, but an excess of either hydrochloric or sulphuric acid dissolves it, forming a brownish yellow liquid, from which ammonia separates it unchanged; by this reaction it may be distinguished from roseine, which dissolves in strong sulphuric acid, producing the green liquid previously mentioned. Caustic alkalies, or ammonia in excess, partially precipitate fuchsine from its salts, but at the same time, dissolve a considerable quantity of it, forming nearly colourless liquids. Acetic acid added to these alkaline solutions restores the colour of the fuchsine, and if the liquids are concentrated, this base precipitates as a red floculent substance.

An alcoholic solution of fuchsine, when evaporated to dryness, leaves the colouring matter as a brittle mass, having a remarkably beautiful golden-green metallic reflection.

M. Béchamp has analysed carefully prepared specimens of fuchsine, and found it to have the formula: $C_{12}H_{12}N_2O$, the hydrochlorate being $C_{12}H_{12}N_2O,HCl$, and the hydrochloroplatinate, which is a purple precipitate, having the formula $C_{12}H_{12}N_2O,HPtCl_3$.

The existence of oxygen in this base is remarkable; because, in many instances, it is produced from agents which do not contain a trace of oxygen; as for example, bichloride of tin and aniline. The presence of oxygen in the product analysed, leads to the idea that it was a hydrate; thus—

$$\underbrace{C_{12}H_{12}N_2O}_{\text{Béchamp's fuchsine.}} = \underbrace{C_{12}H_{10}N_2}_{\text{Anhydrous fuchsine.}} + H_2O$$

This is perhaps, to some extent, confirmed by the fact that iodaniline when heated yields fuchsine:

$$2\ \underbrace{[C_6(H_6I)N]}_{\text{Iodaniline.}} = \underbrace{C_{12}H_{10}N_2}_{\text{Anhydrous fuchsine.}} + 2HI$$

But supposing the fuchsine examined by M. Béchamp, to have been a hydrate, it is remarkable that its hydrochlorate, and more particularly its hydrochloroplatinate, should also be hydrates. But, as our knowledge of this body is as yet but scanty, we must wait for the accumulation of facts before we can form any fixed opinion respecting its constitution.

The compounds investigated by M. Béchamp appear to be uncrystallizable. Sometime back I had upwards of a hundred gallons of a hot aqueous solution of this colouring matter, which had been prepared by means of nitrate of mercury. This solution, on standing until cold, deposited a considerable quantity of the colouring matter in the form of small octahedrons, having a most beautiful green metallic reflection.

Reducing agents decolorize fuchsine; but the oxygen of the atmosphere restores it to its original tint. If an alcoholic solution of fuchsine be left in contact with sulphide of ammonium until decolorized (or nearly so), and then exposed to the atmosphere, its colour is immediately restored; but if it be left to stand for several days, and then subjected to the atmosphere, several hours elapse before it assumes its original colour. Like aniline purple, fuchsine is a very intense colouring matter.

Tannin precipitates both fuchsine and its salts, forming difficultly soluble substances; bichloride of mercury also precipitates this base and its salts, forming double compounds.

When fuchsine is prepared by means of bichloride of tin, and more particularly when nitrate of mercury is used, there are two other colouring matters produced—one possessing an orange and the other a purple colour. It is on account of the presence of the former that some samples of commercial fuchsine possess a scarlet hue. Of this orange colouring matter scarcely anything is known. It is not precipitated from its solutions by alkalies. Of the purple colouring matter also but little is known. It is formed at the same time as fuchsine, but in very small quantity, and is difficult to separate perfectly. Its properties are similar to those of fuchsine. It dissolves in concentrated sulphuric acid, forming a reddish brown solution, from which part of the colouring matter is separated by dilution with water. Hydrochloric acid dissolves it, forming a dirty yellowish-red liquid.

Bleu de Paris.—This is yet another colouring matter, produced under circumstances similar to those which give rise to fuchsine. MM. **Persoz, V. de Luynes,** and **Salvétat** give the following account of its preparation and properties:—

Nine grammes of anhydrous bichloride of tin and 16 grammes of aniline, heated for 30 hours to a temperature of about 180° C., in a sealed tube, produce neither a red nor a violet, but a very pure and lively blue. This blue, which resists acids, is darkened in colour by alkalies; but passes to a groselle violet when submitted to this agent in a concentrated state. It preserves its beauty of colour by artificial light, and it dyes animal fibres of a shade whose beauty leaves nothing to be desired.

This colouring matter crystallizes from its alcoholic solutions in fine needles, having an aspect similar to that of ammoniacal sulphate of copper. It is soluble in water, alcohol, wood-spirit, and acetic acid, but insoluble in ether and bisulphide of carbon. With concentrated sulphuric acid it forms an amber-coloured solution, which water converts into a magnificent blue liquid. Strong nitric acid decomposes it. Chromic acid precipitates it from its aqueous solutions without decomposition. Chlorine destroys it. Sulphurous acid does not decolorize it. I find that sulphide of ammonium is also without action upon it. It is precipitated from its aqueous solutions by alkalies and saline compounds.

Aniline-Green or Emeraldine.—Most chemists who have worked with aniline in the laboratory, must have noticed the peculiar green substance which forms on the outside of the various pieces of chemical apparatus which have been standing in the vicinity of any quantity of this body; this product is aniline-green.

Aniline-green has been known for several years. It may be formed by various processes. One process consists in oxidizing aniline with chloric acid. This is effected by mixing a hydrochloric solution of aniline with chlorate of potassium. It may also be obtained by oxidizing a salt of aniline with ferric chloride. Obtained by either of these processes, it presents itself as a dull green precipitate, which, when dried, assumes an olive green colour. It is insoluble in water, alcohol, ether, and benzole. Sulphuric acid dissolves it, forming a dirty purple-coloured solution, from which it is precipitated unchanged by water. With alkaline solutions it assumes a deep colour, somewhat similar to indigo; but acids restore it to its original tint. The colour of aniline-green is much enlivened by the presence of an excess of acid; but, unfortunately, as soon as this acid is removed, it passes back to its normal colour.

Toluidine, xylidine, and cumidine, yield colouring matters under the influence of oxidizing agents, and also when submitted to the action of reducible chlorides at high temperatures, analogous to those obtained from aniline under similar circumstances; but the results are generally not so good, the colour of the products becoming tinged with brown as the bases get higher in the series.

NITROSOPHENYLINE.—This remarkable body is obtained by the action of nascent hydrogen on an alcoholic solution of dinitrobenzole. It is represented by the formula $C_6H_6N_2O$. It is almost insoluble in water, but soluble in acids and in alcohol, producing crimson-coloured solutions; but its colour is not nearly so brilliant as that of fuchsine. It seems gradually to decompose when kept. I have not tried any experiments with it as regards its dyeing properties.

DINITRANILINE. — Dinitraniline is obtaind by decomposing dinitrophenyl-citraconimide with carbonate of sodium. When pure it crystallizes in yellow tables. It dissolves very sparingly in water, producing a yellow liquid. It has the formula

$$C_6H_5(NO_2)_2N.$$

It does not combine with acids or alkalies, although it appears to be more soluble in acidulated than in pure water.

Silk can be dyed yellow with dinitraniline.

NITROPHENYLENE-DIAMINE, OR NITRAZOPHENYLAMINE.—Dinitraniline, when submitted to the action of sulphide of ammonium, changes into this beautiful base, which crystallizes in red needles, somewhat similar in appearance to chromic acid. It dissolves in water, forming a yellow or orange-coloured solution, like that of bichromate of potassium. Alcohol and ether dissolve it freely. It is not at all like fuchsine in its properties, as it forms salts of a yellowish brown or grey colour, whereas, fuchsine forms crimson salts.

This base possesses the power of dyeing silk a very clear golden yellow colour.

Picric, or Trinitrophenic Acid.—This beautiful acid was discovered by Hausmann as early as 1788. It may be obtained by the action of heated nitric acid upon a great variety of substances. The following are the names of some of them :—indigo, aniline, carbolic acid, saligenine, salicylous and salicylic acids, salicine, phlorizin, cumarin, silk, aloes, and various gum-resins. It is now prepared for commercial purposes from carbolic acid, and also from certain gum-resins.

I have successfully prepared it from carbolic acid on the large scale in the following manner :—As strong nitric acid acts very violently when brought in contact with carbolic acid, I have found it best to use an acid having a gravity below 1·3, so as partially to convert the carbolic acid, and afterwards to boil it in stronger acid to change it into picric acid. On diluting the acid solution, the impure picric acid precipitates. To purify this further, it should be crystallized from boiling water.

When preparing this product for commercial purposes, it is advantageous to let all the nitrous fumes formed in its preparation, together with a certain amount of atmospheric air, pass over a fresh quantity of carbolic acid: this will absorb them, and, at the same time, be converted into nitro- or dinitro-phenic acid, and consequently diminish the quantity of nitric acid required for its manufacture.

In the preparation of picric acid from carbolic acid there is always a quantity of a yellow resinous matter produced, and at times a considerable quantity of oxalic acid. The latter is always produced when the acid which is used to finally convert the carbolic acid, is too weak: for then it rapidly decomposes the picric acid, yielding carbonic and oxalic acids.

Picric acid was introduced as a yellow dye about five or six years since by Messrs. Guinon, Marnas, and Bonney, eminent silk-dyers, of Lyons. Many of the cheap products sold of picric acid are of a brown colour, and consist of impure di- and tri-nitrophenic acids, and sometimes of this crude product and ground turmeric.

ROSOLIC ACID.

Runge first noticed this substance in 1834, when studying creosote; but it was almost lost sight of, until again observed by Dr. Hugo Müller, only a short time since. He accidentally observed that when crude phenate of calcium is exposed to a moist heated atmosphere, as that of an ordinary drying stove, it gradually changes in colour, and assumes a dark red tint. This coloration is due to the formation of rosolate of calcium. (I have lately heard that phenate of sodium undergoes a similar change.) Dr. Müller's mode of preparing rosolic acid from this product, and his description of its properties, are given in his paper published in this Journal, vol. xi, p. 1; it is therefore unnecessary to repeat them.*

Mr. Duppa and myself, when investigating some of the derivatives of acetic acid, found that when phenic acid and bromacetic acid were heated together at 120°C., two products were formed, one possessing all the properties of rosolic acid, while the other had the character of brunolic acid. We also found that a mixture of iodine and carbolic acid, when heated with formic, acetic, butyric, or valerianic acids, produced rosolic acid or a similar substance. A mixture of carbolic acid and iodine did not give a similar result, but a black solid containing iodine.

Rosolic acid has lately been prepared on the large scale, and employed for the purpose of printing muslins. I believe it was the rosolate of magnesium that was employed for this purpose. I do not think it is now used, having been replaced by the more beautiful colouring matter, fuchsine. It was fixed by means of albumin.

COLOURING MATTERS OF QUINOLINE OR CHINOLINE.

Chinoline is found associated with lepidine, cryptidine, and other of the higher nitrile-bases in the basic oils obtained from coal tar, and also in the products obtained by distilling cinchonine with caustic alkalies. It was previously termed *leucoline* or

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[*] See also Tschelnitz (J. pr. Chem. lxxi: 416; and R. Angus Smith, Phil. Mag. (4) xiii, 45; Jahresbericht d. Chem., 1857, p. 447.

quinoline, but the substance described under these two names was found to contain three or more distinct bases. These have been studied by C. Greville Williams, who has applied the name ***chinoline*** to the product which forms the principal part of the impure substance originally termed quinoline. The substance used for the production of colouring matters need not be pure chinoline, as the product originally termed quinoline is of sufficient purity for this purpose.

Cinchonine appears to be the best source of chinoline, yielding, when distilled with excess of caustic alkali, 65 per cent. of this body sufficiently pure for manufacturing purposes.

Chinoline yields three colouring matters—a violet, a blue, and a green. The following is an account of their preparation by Greville Williams:—

In order to procure the blue colour, one part by weight of chinoline is to be boiled for ten minutes with one and a half parts of iodide of amyl. The mixture from being straw-coloured becomes deep reddish brown, and solidifies on cooling to a mass of crystals. This product of the reaction is to be boiled for ten minutes with about six parts of water, and, when dissolved, filtered through paper. The filtered liquid is to be gently boiled in an enamelled iron pan over a small fire, and excess of ammonia gradually added. The ebullition may be prolonged with advantage for one hour, the evaporation of the liquid being compensated for by the gradual addition of weak solution of ammonia. The latter may be prepared by the admixture of equal volumes of ammonia of density 0·880 and distilled water. The hour having elapsed the whole is allowed to cool, when the colour will almost entirely have precipitated, leaving the supernatant liquid nearly colourless. On pouring the fluid away (preferably through a filter, in order to retain floating particles of colour) the dish will be found to contain resinous looking masses which dissolve readily in alcohol, yielding a rich purplish-blue solution which may be filtered and kept for use.

The colour prepared as above is, as has been said, of a purplish tint, but if a purer blue be required, the following modification is to be resorted to. The filtered aqueous solution of hydriodate of amyl-chinoline is, as before, to be brought to the boiling temperature, but instead of adding ammonia, a solution of caustic potash, containing about one-fifth of its weight of solid potash, is to be substituted. The addition is to be continued at intervals until three-fourths as much potash has been added as is equivalent to the iodine in the iodide of amyle used. The fluid may, after a quarter of an hour's ebullition, be filtered to separate the resinous colour. The product is a gorgeous blue with scarcely any shade of red. On adding the other fourth of potash to the filtrate while gently boiling, a black mass will be precipitated containing all the red, which otherwise would have been mixed with the blue. This mass dissolves readily in alcohol, yielding a rich purple solution, containing, however, an excess of red. The alcoholic solution on filtration leaves on the filter a dark mass soluble in benzole, and, as sometimes prepared, affording a brilliant emerald-green solution of great beauty. It is not always easy to obtain this green colour.

The properties of chinoline-violet and chinoline-blue are, as far as I have been able to ascertain, identical. They are resinous substances which present a coppery appearance by reflected light, but when in very thin layers, appear of a violet or blue colour by transmitted light. They are bases, and dissolve in acids, forming pale red solutions, which ammonia restores to their original colours. They are slightly soluble in hot water. Tannin precipitates them from their aqueous solutions, apparently forming an insoluble compound. Reducing agents do not affect their shade of colour.

Chinoline green is described by Greville Williams as having a brilliant emerald-green colour of great beauty. I have observed that when chlorine is passed through an alcoholic solution of chinoline blue, it changes into a green; but whether this is the green spoken of by Williams, I am unable to state.

NAPHTHALINE COLOURS.

The beautiful hydrocarbon, naphthaline, which has yielded such a long category of substances to the chemist, has, up to the present time, yielded nothing of practical importance to the dyer. From it the following coloured derivatives have been obtained, namely, *chloroxynaphthalic acid, perchloroxynaphthalic acid, carminaphtha, ninaphthalamine, nitrosonaphthalin, naphthamein,* and a body of a purple *colour.*

CHLOROXYNAPHTHALIC AND PERCHLOROXYNAPHTHALIC ACIDS.—These acids were discovered by Laurent. They are produced by digesting their chlorides, namely, the chloride of chloroxynaphthyl and the chloride of perchloroxynaphthyl with an alcoholic solution of hydrate of potassium. They appear to be very difficult substances to obtain in quantity. I have not obtained satisfactory results when endeavouring to prepare them; they have the formulæ $C_{10}(H_5Cl)O_3$ and $C_{10}(HCl_5)O_3$ respectively. They are regarded with great interest, as being very closely allied to alizarine, the colouring matter of madder: in fact, they are viewed as chloralizaric acids; that hypothesis is based upon the idea of alizarine having the formula $C_{10}H_6O_3$; but it happens very unfortunately for this theory that the formula of alizarine itself is still a disputed point.

Chloroxynaphthalic acid is of a yellow colour; its salts are yellow, orange, or crimson, and are described as possessing great beauty. Silk dyed with the ammonium-salt acquires a good golden-yellow colour, little affected by light.

CARMINAPHTHA.—This colouring matter was also discovered by Laurent. It is obtained by heating naphthaline with a solution of bichromate of potassium, and then adding sulphuric or hydrochloric acids. It is described as a fine red substance soluble in alkalies, but precipitated from its alkaline solutions by means of acids. I have never obtained this product when oxidizing naphthalene.

NINAPHTHALAMINE.—Ninaphthalamine is the name given to a remarkable base which was noticed by Laurent and Zinin; but nothing was known of its nature until it was re-subjected to investigation by Mr. Wood, who has both described and analysed it and some of its salts; its formula is, $C_{10}(H_8NO)N$, or naphthalamine in which H is replaced by NO. It is obtained by passing sulphuretted hydrogen through a boiling solution of dinitronaphthaline in weak alcoholic ammonia. The details of the preparation are described in the 12th volume of this Journal, page 154. It has a bright red colour, but I do not think it would be of any value as a dyeing agent, even if it could be obtained cheaply.

NITROSONAPHTHALIN.—This peculiar body is a product of the action of nitrous acid on naphthalamine. It is prepared by mixing a solution of hydrochlorate of naphthalamine with nitrite of potassium. From this mixture it separates as a redish-brown precipitate. This, when washed with water on a filter and then dried, is dissolved in alcohol, filtered, and evaporated to dryness on the water-bath. Thus prepared, it is a crystalline dark-coloured substance, having a greenish metallic reflection. It is soluble in alcohol and also in benzole, forming orange-red solutions.

When acids are added to an alcoholic solution of nitrosonaphthalin, it immediately assumes a most beautiful purple or violet colour as fine as any of the aniline purples. Alkalies restore it to its original colour. Silk may be dyed a beautiful purple shade with this substance, provided a certain quantity of hydrochloric or sulphuric acid be present; but what is most unfortunate is, that when the silk thus dyed is rinsed in water, the colour immediately passes back to that of pure nitrosonaphthalin, and, also, that the amount of acid required to keep up the purple shade, if left in the silk, rots it in a few days. Could this purple be fixed, nitrosonaphthalin would become a cheap and most useful dye.

I have endeavoured to produce a sulpho-acid of nitrosonaphthalin, thinking that if such a compound could be obtained, it would possess the purple colour, because it would be an acid itself. But although sulphuric acid does dissolve it, forming a blue solution, no combination takes place. I also endeavoured to produce this desired result by treating sulphonaphthalamic acid with nitrous acid, but obtained only nitrosonaphthalin, the acid of the sulphonaphthalamic acid having apparently separated.

NAPHTHAMEIN.—Piria[*] observed that naphthalamine and its salts produce blue precipitates, afterwards becoming purple, when brought in contact with perchloride of iron, terchloride of gold, nitrate of silver, and other oxidizing agents. This product of oxidation he terms naphthamein. Silk and cotton may be dyed with it; but the colour of this compound is so inferior as to render it useless as a dyeing agent.

Naphthalamine, when heated with anhydrous bichloride of tin, yields a purple colouring matter, which is insoluble in water, but insolubility renders it difficult to use, and its colour is not nearly so good as that of aniline purple.

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[*] Ann. Ch. Phys. (3) xxxi, 217.

TAR RED.

This colouring matter was discovered by Mr. Clift, of Manchester, in 1853. It is obtained by exposing a mixture of the more volatile parts of the basic oils of coal tar and hypochlorite of calcium to the air for about three weeks. Of the pure colouring matter I know nothing, except that with tannin it forms an insoluble or difficultly soluble substance, and that with different mordants, it yields different colours.

Professor Calvert has been kind enough to send me a leaf of his Note-book containing the results of different experiments he made upon this colouring matter, which show that the colours obtained from this product are anything but good.

It seems probable that this colouring matter is derived from the pyrrole.

AZULINE.

This substance, which is a beautiful blue dye, has been introduced into England within the last six months. It was discovered by Messrs. Guinon, Marnas, and Bonney, of Lyons, who keep the process for its preparation a secret. It is obtained from coal-tar; but from which of its numerous derivatives is not known.

This colouring matter is a brittle uncrystallizable body, possessing a coppery metallic reflection. It is very difficultly soluble in water, but soluble in alcohol, producing a magnificent blue solution, having but a slight tinge of red. With concentrated sulphuric acid, it forms a blood-red liquid, which when poured into an excess of water, precipitates the colouring matter unchanged. Dilute acids have no effect upon azuline. Its alcoholic solution mixed with an alcoholic solution of hydrate of potassium also changes to a dull-red colour. This, when diluted with water, forms a purple liquid, which is gradually restored to its original blue colour by hydrochloric acid. With excess of ammonia the solutions of azuline change to a reddish-purple colour. This is soluble in alcohol. I have made several experiments with it as a dyeing agent, but have not obtained any satisfactory results. Its ammoniacal solution treated with sulphide of ammonium, gradually assumes a pale yellowish-brown colour. Iodine destroys the colour of azuline.

In colour it is not quite so fine as chinoline blue, though far superior to Prussian blue.

Application of Coal-Tar Colours to the arts of Dyeing Silk and Wool.

Silk and wool can be dyed with all the coal-tar colours, with the exception of the rosolates, these fibres possessing in most cases a remarkable affinity (if I may so speak) for these colouring matters. Many of them, as aniline-purple and violine, are taken from their aqueous solutions so perfectly by these substances, that the water in which they were dissolved is left colourless. In fact, silk and wool take them up so rapidly that one of the great difficulties the dyer has to contend with is to get the fibres dyed evenly.

Dyeing Silk with Aniline Purple, Violine, and Roseine.—One process is applicable for dyeing silk with either of these colouring matters, and it is a very simple one. The alcoholic solution of the colouring matter required is to be mixed with about eight times its bulk of hot water, previously acidulated with tartaric acid, and then poured into the dye bath, which consists of cold water slightly acidulated; after being well mixed, the silk is to be worked in it until of the required shade. If a bluer shade than that of the colouring matter is required, a little solution of sulphindigotic acid may be added to the dye-bath, or the silk may previously be dyed blue with Prussian blue or any other blue, and then worked in the dye-bath.

To Dye Silk with Fuchsine, Picric Acid, Chinoline blue, and Chinoline violet.—This process is still more simple than the above, as it is merely necessary to work the silk in cold aqueous solutions of these colouring matters. With fuchsine or picric acid, a little acetic acid may be used; but with chinoline colours, acids must be avoided. With picric acid, a very clear green colour may be obtained by adding a little sulphindigotic acid to the dye-bath.

I may mention that the colour of violine is not so fine as that produced by aniline purple and indigo blue; also that roseine is not so good a colour as fuchsine.

To Dye Silk with Azuline.—The dyeing of silk with this colouring matter is far more difficult than with the preceding, requiring to go through two or three different processes. This difficulty I believe arises from the unsolubility of azuline in water.

The process generally employed is to work the silk in a solution of the colouring matter in water acidulated with sulphuric acid, and when of sufficient depth, to raise the temperature of the dye-bath to the boiling point, and work the silk in it again; after this the silk is well rinsed in water, until free from acid, and worked in a bath of soap lather. It is then again rinsed and finished in a dilute acid bath.

To dye Wool with Aniline purple, Violine, Roseine, Fuchsine, and Chinoline colours.—This operation is generally conducted at a temperature of 50° or 60° centigrade, and the dye-bath is composed of nothing but a dilute aqueous solution of the colouring matter required. Acids should be avoided, or only a very small quantity used, as the resulting colours are not so fine when they are employed.

METHODS OF DYEING COTTON WITH COAL-TAR COLOURS.

When Aniline purple was first introduced, considerable difficulty was experienced in dyeing cotton so as to obtain a colour that would resist the action of soap. Aniline purple is absorbed by vegetable fibres to a certain extent, and very beautiful colours may be obtained by simply working cotton in its aqueous solutions, but when thus dyed, the colours will not stand the action of soap. I have tried the use of tin and other mordants, but without any satisfactory result.

In 1857, Mr. Puller, of Perth, and myself, simultaneously discovered a process by which this colouring matter could be fixed upon vegetable fibres so as to resist the action of soap. This process is based upon the formation of an insoluble compound of the colouring matter with tannin and a metallic base in the fibre.

To effect this, the cotton has to be soaked in a decoction of sumach, galls, or any other substance rich in tannin, for an hour or two, and then passed into a weak solution of stannate of sodium, and worked in it for about an hour; it is then wrung out, turned in a dilute acid liquor, and then rinsed in water. Cotton thus prepared is of a pale-yellow colour, and has a remarkable power of combining with aniline purple. The above process may be modified, as for example, the stannate of sodium may be applied to the cotton before the tannin, and alum may also be used in the place of stannate of sodium. To dye this prepared cotton with aniline purple, it is only necessary to work it in an acidulated solution of the colouring matter; when thus prepared, the cotton will absorb all the colouring matter of the dye-bath, leaving the water perfectly colourless. It has been found that cotton thus prepared can be dyed with any colouring matter that forms an insoluble compound with tannin. It is therefore used for dyeing with roseine, violine, fuchsine, and chinoline colours.

Cotton may also be dyed a very good and fast colour by mordanting it with a basic lead-salt, and then working it in a hot solution of soap, to which aniline purple has been added.

Oiled cotton, such as is used for dyeing with madder, is also used in dyeing these colours. Cotton simply oiled, and before mordanted with alum and galls, absorbs coal-tar colouring matters with great avidity, producing very fine shades. Oiled cotton mordanted with alum and galls also combines rapidly with these colouring matters: but as the colour of the prepared cotton, is generally rather yellow, it interferes sometimes with the beauty of the result.

Cotton is sometimes washed with albumin, which is coagulated by the action of steam, and the albumin, which covers the cotton, dyed in the usual manner.

I may mention that violine, roseine, fuchsine, and also the chinoline colours, combined with unmordanted vegetable fibres as well as aniline-purple. Picric and rosolic acids are not applicable for dyeing cotton.

PRINTING CALICO WITH COAL-TAR COLOURS.—The process generally employed for printing with these colouring matters is simply to mix them with albumin or lacterine, print this mixture on the fabric, and then to coagulate the albumen or lacterine by the agency of steam.

Mr. Grey, of the Dalmonach Print-works, and myself, discovered the first process of applying these substances to fabrics in a different manner to the above.

It consisted in forming a basic carbonate, or an oxide of lead, on those parts of the cloth which were to be coloured, and then working the cloth thus prepared in a hot lather containing the colouring matter. Where the cloth was mordanted with the lead-compound, the colouring matter was absorbed; but where immordanted it was left white, because pure cotton is not dyed with these colouring matters in the presence of soap. This process was intended for the application of aniline-purple, for, at the period of this discovery, the other coal-tar colours were unknown. Colours dyed by this process were very pure; but it had many disadvantages which have caused it to be disused.

Lately the process previously described for dyeing colours upon cotton prepared with tannin, has been applied to calico-printing. It consists in printing tannin upon the fabric previously prepared with stannate of sodium, and then dyeing it in a hot dilute acid solution of the colouring matter (in the case of chinoline colours acid must not be used); by this means, the parts of the fabric which are covered with tannin are dyed a deep colour, but the other parts are only slightly coloured. These are cleared by means of well-known processes.

This method of applying these colouring matters is also modified by printing a compound of the colouring matter required and tannin on the prepared cloth, instead of the tannin only, and then steaming the goods.

METHOD OF APPLYING ANILINE GREEN TO FABRICS.—This process, which is interesting, as being the first example of the production of coal-tar colours on the fabric itself, was proposed by Professor Calvert: it is very simple. The design is to be printed on the cloth with a thickened solution of chlorate of potassium, dried, passed through a solution of an aniline salt, again dried, and allowed to hang in a moist atmosphere. In the course of two or three days, the colour will be fully developed. The colour thus produced may be changed into a dark blue by the agency of soap or an alkaline liquid. This process is very inexpensive; the amount of aniline required being very small.

APPLICATION OF NITROSONAPHTHALIN.—If cloth is printed with a thickened solution of a salt of naphthalamine, dried, and then passed through a solution of nitrite of potassium, nitrosonaphthyline will rapidly make its appearance as a reddish-orange colour; but unfortunately the colour thus obtained will not resist the action of soap.

Many of the coal-tar colours, when viewed by artificial light, are very much modified in tint; and some of them, when compared with similar colours of vegetable origin by daylight, appear of totally different tints by gaslight. The latter case is remarkably illustrated by aniline-purple and archil.

If two silk patterns are dyed, one with aniline purple, and the other with archil, of exactly the same shade of colour when seen by daylight, the colour of the archil pattern when viewed by artificial light, will appear several shades redder than that of the aniline purple.

Dr. Gladstone has examined solutions of these two colouring matters in a hollow wedge by means of the prism, and he finds that a very thin stratum of aniline-purple attacks the spectrum in the yellow (just beyond D), giving rise to a blue-purple colour; and that, as the intensity of the solution increases, the absorption gradually extends very slowly on the less refrangible side, but rapidly on the more refrangible side, till the green entirely disappears, and eventually the true blue.

In the case of archil, the violet and blue rays are absorbed by a strong solution of this colouring matter, though it still permits the extreme *red* ray to pass with great facility: therefore, considering the abundance of red in oil or gas-light, it is not surprising to find that archil colours appear redder by artificial light than those of aniline purple.

The colour of the three coal-tar blues, ***bleu de Paris***, ***azuline***, and *chinoline-blue*, when viewed by gaslight, are considerably modified. The *bleu de Paris* appears blue; azuline, a heavy blueish violet; while the chinoline-blue assumes a beautiful violet tint having rather a cast of red.

Dr. Gladstone has also kindly examined these three colouring matters, and gives the following account of his results:—These three blues, in common with aniline purple, attack the spectrum in the yellow (near D), and as the intensity of the colour increases, the absorption extends, especially on the more refrangible side, till the *green* is swallowed up. At the same time the *orange* is absorbed, while the extreme red is transmitted freely.

In the *bleu de Paris* there is an additional band of absorption in the orange, when very weak solutions are examined; but this is soon merged in the greater band extending from the yellow as the solution increases in intensity.

Strong solutions of azuline absorb the yellow, green, blue, and violet in regular order; but the chinoline blue absorbs the violet when not very deep, and allows the blue to pass for some distance further, after which the *red* alone passes.

Dr. Gladstone states that the chinoline blue is one of the most beautiful dichromatic substances he knows; when viewed in a hollow wedge, with the prism, it passes gradually from a clear blue to a fine red.

Of the numerous colouring matters of which I have briefly spoken, there are only four that are at present employed by the dyer and printer; namely: aniline purple, fuchsine, picric acid, and azuline; but I think it probable that others of them will soon be introduced, such as the bleu de Paris. Nitrophenylene-diamine might also be used for silk-dyeing, as its colour is good, and it resists the action of light well.

Unfortunately the chinoline colours, though very beautiful, are most fugitive. There has been an endeavour to introduce the chinoline blue of late; but, although a considerable quantity of silk was dyed with it at first, it is now scarcely used, because, when exposed to the sun for two or three hours, the dyed silk becomes bleached.

Aniline purple resists the light best. Fuchsine and alpha aniline purple soon fade, especially when on cotton. Azuline and bleu de Paris are not easily acted upon by light when on silk.

When the colouring matters of coal-tar were first introduced, there was great fear that the workmen engaged in their manufacture would suffer in health. All I can say is, that during the few years I have had to do with this branch of manufacture, there has not been a single case of illness among the workmen that has been produced by any of the operations carried on for the production of *aniline purple*.

Researches on the Constituents of Gastric Juice.

BY WILLIAM MARCET, M.D., F.R.S.

IN the spring of last year, being engaged with some investigations on gastric juice, I was induced to examine a sample of this secretion in Soleil's saccharimeter; when, to my astonishment, I observed it to act strongly on the polarized ray, rotating the plane of polarization of light to the left. I then undertook a series of investigations in order to determine which was the constituent of gastric juice possessed of the above optical property, and to what amount it exhibited this rotating power in the saccharimeter: these researches form the subject of the present communication.

The gastric juice used in my experiments was procured from two dogs, in whose stomachs I had established permanent fistulæ. One of these animals had been operated on in December, 1859; in the following month of October (1860), finding my supply of gastric juice insufficient, I established a gastric fistula in the second dog. The animals have both been in very good health ever since.

The gastric juice was obtained after allowing the dogs to fast for thirty or forty hours, and then feeding them with soft bones (*i.e.*, bones containing cartilage) boiled and cut up, or pieces of the windpipes of oxen or sheep—those of the ox being boiled (though not softened), the tracheæ of sheep being usually given raw. Windpipes were most frequently used, as they produced a good supply of the secretion, without causing any gastric disturbance. The secretion was collected from time to time during an hour or an hour and a-half after the animals had been fed, and from two to five ounces were usually obtained from each of them.

The fluid was in every case turbid when first extracted, containing, especially, fat. When the amount of substance in suspension was great, I found it advisable to begin by straining the gastric juice through calico; at all events, it had to be filtered through paper over and over again, until sufficiently clear to admit light freely through a layer of the fluid equal in thickness to the length of the saccharimeter-tube.

Every sample of gastric juice obtained under the above-mentioned circumstances from either of the dogs, rotated the plane of polarization of light to the left to an extent indicated by from 15° or 20° to 40° of Soleil's saccharimeter. The acidity of the fluid, which was frequently determined, varied in 10 c.c. from 0·011 to 0·039 gramme—these numbers representing the amount of potash necessary to neutralise 10 c.c. of the gastric juice, equivalent to from 0·085 to 0·303 per cent. of hydrochloric acid. This degree of acidity, although rather lower, agrees with that obtained by Bidder and Schmidt (*Verdauungssäfte*, &c.), which is from 0·1708 to 0·3353 per cent. of hydrochloric acid.

My first impression was, that the optical properties of gastric juice were due to its acid. I therefore examined at once in the saccharimeter a sample of lactic acid prepared from sugar of milk; but it had no action on polarized light. Next, some lactic acid was extracted from flesh according to Liebig's process; this again exhibited no optical property in Soleil's polariscope.

After some consideration, I determined upon trying the separation of the constituents of gastric juice by means of hydrated oxide of lead, with the view of examining the action of light on the substances precipitated, and on those not precipitated, by this agent. Having boiled a sample of the secretion with hydrated oxide of lead in excess, and filtered the mixture, a fluid was obtained having a marked alkaline reaction, but containing only a comparatively small quantity of lead. I submitted this fluid to examination in the saccharimeter, and found it to act powerfully on polarized light. This proved that I had been mistaken in supposing that the action of gastric juice on polarized light was owing to its acid constituent.

Finding that the alkaline filtrate from the boiled mixture of gastric juice and hydrated oxide of lead contained the substance I was in quest of, I naturally believed it to be an alkali, and for a long while I endeavoured to isolate it under the form of crystals or of an insoluble salt. Failing in this, and finding that the substance was precipitated amorphous by alcohol, I determined upon availing myself of this means to prepare it in as pure a condition as possible; and, finally, I obtained a body having a definite rotating power on polarized light, and possessing the chemical properties of the substance known to result from the digestion of albuminous and gelatinous food, which Lehmann has called *peptone*.

Preparation.—The following is the process I adopted for the preparation of this substance, which, however, I could never obtain perfectly free from inorganic matters.

The gastric juice, excited, collected, and filtered as above, was boiled in order to coagulate the albumen (when, apparently, according to Lehmann,* the pepsine is also precipitated), and then filtered, to be mixed with three times its bulk of commercial alcohol, 56 over proof (sp. gr. 842). A few hours later, or still better, the next day, the fluid was filtered from the *precipitate* which had formed, and then distilled or concentrated on the water-bath; the composition of the precipitate was subjected to a special inquiry. The residue from the distilled or concentrated fluid had a syrupy consistence; it was treated with a small quantity of sulphuric acid diluted with four or five times its bulk of water and added cold, the capsule containing the syrupy residue being at the time floated on cold water, to prevent any rising of temperature from the action of the acid; alcohol was next mixed with the thick acid fluid until the gelatinous precipitate it induced had ceased to increase, the mixture being at the same time agitated with a glass rod, to which much of the precipitate became attached. The gelatinous substance was now thoroughly washed with alcohol, and then dissolved in water, yielding a solution turbid from the presence of sulphate of lime, which had to be removed by filtration. I now boiled the clear fluid with an excess of hydrated oxide of lead, and after allowing the mixture to remain undisturbed till the next day, it was filtered. The filtrate was obtained clear, although on some occasions it had to be filtered repeatedly; it was then ascertained, with sulphuric acid and sulphide of ammonium, to be free from lead: it had an alkaline reaction, more or less strong, and contained a little lime with traces of soda-salts. I have succeeded, to a great extent, in getting rid of the lime, by adding cautiously to the fluid a very weak solution of oxalic acid, until it became nearly neutral, and then filtering. I also feel confident that the presence of a certain quantity of alcohol in the acid solution, previous to boiling it with oxide of lead, causes the precipitation of nearly all the lime as sulphate; indeed, I have quite recently ascertained that the acid solution in question, mixed with an equal bulk of alcohol, 56 o.p., in the course of two or three days, deposited the whole of its lime as sulphate; the fluid, after evaporation in order to get rid of the alcohol, giving no precipitate with ammonia and oxalate of ammonia, yet the amount of alcohol added had precipitated an insignificant quantity of the polarizing substance. In some instances I found the filtrate from the lead precipitate nearly free from lime, which I attribute to the action of the alcohol which had remained mixed with the gelatinous substance after it had been washed with this fluid, or to all the lime having been precipitated at first by the addition of alcohol to the gastric juice: in these instances it was not necessary to use oxalic acid.

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* Berichte über die Verhandlungen der Königlich-Sächsischen Gesellschaft de Wissenschaften zu Leipzig, 1849.

The alkaline filtrate from the lead precipitate, as free from lime as possible, was concentrated to the consistence of a thin syrup, and finally precipitated by alcohol, or a mixture of alcohol and ether. After a day or two the fluid, now become clear, was decanted, leaving a perfectly homogeneous substance, transparent, colourless, or nearly so, adhering to the sides of the receiver under the form of a thick, tenacious syrup,.which was dried. The dry substance was very brittle, and exhibited no signs of crystallization; it could be easily scraped off from the sides of the receiver, from which it partly separated in scales; and, being very hygroscopic, had to be preserved in carefully-closed bottles.

Remarks on the above method of investigation.—In every case where gastric juice was obtained, as stated above, it yielded a precipitate by boiling. I made some experiments to determine whether the removal from gastric juice of the substance thus precipitated diminished its action on polarized light; but, on examining the fluid in Soleil's polariscope, before and after the precipitation, I could not discover any loss of its optical properties. When alcohol 56 o.p. (sp. gr. 842) is mixed with clear gastric juice obtained as stated above, which has been boiled and filtered, no turbidity or precipitate takes place until about an equal bulk of alcohol has been added. A further addition of alcohol causes a turbidity, and when the volume of mixture is equal to four times its original bulk, a cloudy precipitate gradually forms, leaving a clear fluid; but the next day the fluid may again have become turbid from the formation of a further quantity of the precipitate. This precipitate was collected on a filter, and, after being washed with a mixture of alcohol and water, was subjected to examination. I was surprised at finding it but partly soluble in water, yielding an acid solution; this solution acted, more or less, on polarized light, but much less than the original gastric juice, showing that some of the polarizing substance (if I may so call it) had been precipitated by the alcohol. For instance, a sample of eight ounces of gastric juice, showing 32·5° in the saccharimeter, being treated with three times its bulk of alcohol, gave a precipitate which exhibited in an aqueous solution measuring two ounces, 13·5°; or a quantity of the polarizing substance in eight ounces of gastric juice, equivalent to 260°, lost a proportion equivalent to 27° by precipitation with three times its bulk of alcohol 56 o.p. This aqueous solution acting slightly on polarized light was also examined with respect to its inorganic salts; for this purpose, after evaporation to dryness, the residue was incinerated, and the ash was found to consist of phosphate of lime, with a little sulphate of lime: the addition of hydrochloric acid emitted no carbonic acid. I also examined the part of the precipitate insoluble in water, after it had been thoroughly washed with distilled water. It dissolved readily in gastric juice, but failed to increase its polarizing power. In one experiment, where I used the precipitate obtained from no less than fourteen ounces of gastric juice, and dissolved this in one ounce of the secretion showing 23°, this solution gave 24° when examined. As an increase of only 1° is not worth taking into account, it is obvious that the precipitate insoluble in water did not increase the optical property of gastric juice when dissolved in the secretion. The precipitate under our present consideration, insoluble in water, was incinerated, and I found it still contained a comparatively large quantity of organic matter. When burnt to ashes, this inorganic residue contained carbonates, as shown by the ready evolution of carbonic acid on the addition of hydrochloric acid,—although, previous to the incineration, no carbonic acid could be obtained; therefore, a carbonate had been formed by the ignition, showing that the precipitate had contained a compound of an organic and inorganic substance. The ash was found to consist of phosphate and carbonate of lime, with traces of sulphate of lime. On considering the organic substance precipitated by alcohol in gastric juice and insoluble in water, it appears to bear a great analogy to the *parapeptone* of Meissner, a substance discovered by this chemist among the products of digestion of albumen.* Parapeptone is obtained by neutralising with potash a solution containing hydrochloric acid and pepsine, after it has been used for the artificial digestion of albumen, this substance (parapeptone) being, under these circumstances, precipitated. It may be surmised that the compound of lime and parapeptone, when present in gastric juice, is precipitated by the addition of alcohol to the secretion, and then by filtration it will lose much of the acid which kept it in solution in the gastric juice, so that when washed with water, the aqueous fluid is no longer sufficiently acid to dissolve it, and, therefore, it remains on the filter. I found this substance not only soluble in gastric juice, but also soluble in dilute acetic and hydrochloric acids, which bears out this view.

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* Zeitschrift für Rationelle Medicin, series 3, vol. vii.

It will now be readily understood why I have in every case precipitated the gastric juice with alcohol, for by so doing I removed the whole, or, at all events, the greater portion of the parapeptone (if it be this substance), and also a quantity of phosphate of lime, which would have interfered, more or less, with the subsequent operations; although by so doing it was impossible to avoid the loss of a small quantity of the polarizing substance.

After freeing the solution from alcohol by distillation, and concentrating the fluid until it assumed a syrupy consistence, I added to it a very small quantity of a mixture of sulphuric acid with four or five times its volume of water. This was done with the view of transforming all the inorganic bases into sulphates, and setting free every organic and inorganic acid which might be present. By washing the gelatinous precipitate with alcohol, nearly the whole of the soda was removed; and on several occasions, especially during cold weather, I observed fine crystals of sulphate of soda in the alcoholic fluid a day or two later. If too much sulphuric acid was added to the syrupy fluid, the subsequent addition of alcohol failed to produce the gelatinous precipitate, when, of course, the whole operation was lost; in these cases, nothing more than a turbidity occurred. The formation of the gelatinous precipitate by the action of alcohol on the acid aqueous solution, and the washing of the precipitate with alcohol, was the cause of a considerable loss of the polarizing substance, which could not, however, be avoided.

The boiling with hydrated oxide of lead I believe to be indispensable to get rid of the sulphuric acid, the phosphoric acid, and other acids which had remained adherent to the gelatinous precipitate, and also perhaps of any pepsine which may have escaped precipitation in the former operations. By boiling the mixture for about three quarters of an hour, and then allowing it to remain undisturbed till the next day, it yields a filtrate which can be obtained quite clear with comparative ease, and perfectly free from lead; showing that the whole of the acids of the gastric juice have been removed, obviously from the formation of basic salts. It sometimes happens, however, that some sulphates escape the action of the oxide of lead, and find their way into the solution, which now only contains the polarizing substance, with a small quantity of lime, soda, and sulphuric acid. I constantly found this solution more or less alkaline.

The treatment with oxide of lead is another source of loss of the polarizing substance; indeed, a large proportion of it remains in the lead precipitate. The following experiments show to what extent hydrated oxide of lead may precipitate the substance under consideration. Eight ounces of gastric juice were found to show 32·5° rotation in the saccharimeter; three times this bulk of alcohol was added, and the precipitate being the next day separated by filtration, was washed with water. This aqueous solution, measuring two ounces, was examined in the saccharimeter, and showed 13·5°. The alcoholic fluid was mixed with hydrated oxide of lead, and evaporated on the water bath to get rid of the alcohol; the next day this fluid was filtered, and the filter washed till the washings were no longer alkaline. The volume of the fluid amounted to 31½ ounces. I added half an ounce of water, and then examined the solution in the saccharimeter; it showed 7°. Now, if none of the polarizing substance had been lost by the evaporation in presence of oxide of lead, and subsequent filtration, the number of degrees found by observation in the saccharimeter ought to have been 10·6°, while, in fact, it was only 7°, a loss of about one third had, therefore, been experienced.

In a second experiment, a solution of the dry substance was prepared in 1½ ounce of distilled water, which showed in the saccharimeter between 15° and 15·5°. This solution was boiled for twenty minutes with hydrated oxide of lead, and again the next day for forty minutes; two days afterwards the fluid was filtered, and the filter washed with distilled water until the filtrate contained only a very small quantity of solid matters. The solution, concentrated to 1½ ounce, showed 11° in the saccharimeter; consequently about one-third of the substance had again been lost in the lead precipitate. As it might be objected, however, that the substance I am alluding to may possibly be decomposed by the mere boiling of its aqueous solution, and not taken up by the lead, I dissolved a sample of it in one ounce of distilled water, which solution showed 4·5° in the saccharimeter. The fluid was boiled for one hour, water being added to replace that which had evaporated; it was made up to one ounce, and examined, when it showed again 4·5°; consequently the substance is not decomposed under these circumstances. The next day the solution had become decidedly hazy, and the observation with the saccharimeter more difficult; still it was seen to deviate the polarized ray to between 4° and 5°; consequently no appreciable amount of the substance dissolved had been decomposed by putrefaction, although the temperature of the air was very high during the whole of the experiment.

I found the polarizing substance to exhibit the chemical properties of Lehmann's peptone; they were as follows:—

Properties.—The substance when dry is brittle, non-crystalline, very transparent, and nearly colourless; it attracts moisture by exposure to the air, becoming a viscous mass. It is very soluble in water, and is precipitated from this solution by the addition of alcohol, and more completely so by a mixture of alcohol and ether. Its aqueous solution has the property of rotating the plane of polarization of light to the left. Four observations made, in order to determine the extent of this rotating power, with different weighed samples of the compound dissolved in 25 cubic centimetres of water, yielded, for 1° of Soleil's saccharimeter, 0·020 grm., 0·023 grm., 0·027 grm., 0·029 grm.; average 0·024 grm. Samples belonging respectively to the same specimens as those examined in the instrument were burnt in order to determine the weight of their ash; and this was subtracted from the weight of the corresponding substance employed for the determination of its optical properties. Therefore, 0·024 grm. of the substance under consideration, or a weight closely approximating to that dissolved in 25 c.c. of distilled water, gives 1° rotation to the left in Soleil's saccharimeter. I need hardly add that the action of a solution of the substance on the saccharimeter is perfectly proportioned to the strength of the solution; this, however, I determined by actual experiment.

The substance exposed to heat burns away almost entirely, leaving small and varying proportions of ash. With tannic acid, its solution yields an immediate and abundant precipitate; it is not precipitated by nitrate of silver, and bichloride of mercury induces in its solutions a slight turbidity. Neutral acetate of lead, in some cases, gave no precipitate; in others, precipitates more or less abundant were produced; these precipitates were evidently accidental, since, with some specimens, I failed to obtain a trace of turbidity on the addition of neutral acetate of lead; and in others the turbidity was but very slight. When this reagent had exerted no action, the addition of a few drops of ammonia to the solution of this salt, without impairing its transparency, caused a precipitate to appear in the solution of the compound under consideration, just as in the case of peptone. Basic acetate of lead gave a precipitate which in most instances was soluble in an excess. I have recently obtained a sample of the polarizing substance which, when dissolved in water, yielded no precipitate with neutral acetate of lead, and with basic acetate of lead, a precipitate soluble in an excess, behaving, therefore, precisely like peptone. The aqueous solution is not precipitated by alkalies or mineral acids.

With respect to its chemical composition, the substance under consideration contains both nitrogen and sulphur. Dissolved in water, it readily undergoes spontaneous decomposition, especially in summer, when, after two or three days, the fluid becomes turbid, and shortly afterwards begins to emit a putrid smell.

In addition to this substance possessing the chemical properties of peptone, I may observe, that the method adopted for its preparation is precisely that which would yield peptone, and this substance must exist in gastric juice, unless every precaution be taken to obtain the secretion perfectly free from the products of digestion.

In order to control the above chemical results, and determine with every degree of certainty, whether the polarizng constituent of gastric juice is secreted in the stomach, or is actually a product of digestion, I have obtained gastric juice after washing out of the stomach all that it contained, and then again exciting the secretion by causing the dog to swallow fragments of bones from which the flesh had been carefully picked. On two other occasions, with the view of avoiding even the possibility of the substance given to the animal undergoing digestion, I used small silicious pebbles instead of bones. When the secretion was excited by fragments of bones, I obtained, in two experiments, samples of gastric juice which acted slightly on polarized light, both showing 7°. In my two experiments with the pebbles, I obtained no rotation at all; the secretion contained, therefore, none of the substance under consideration, proving thereby, that it is not secreted with the gastric juice, and consequently that its invariable presence in the animal fluid, when excited by means of wind-pipes or soft bones, must be the result of some process of digestion.

The next point of importance and interest was to ascertain which is the substance transformed in the stomach into polarizing peptone. I am engaged at present with this part of the investigation. So far, I have obtained proofs that cartilaginous structures, such as the trachea (oxen and sheep), and also bones containing cartilage, yield, under the action of gastric juice, the substance in question. The following are the principal experiments from which this result is derived.

Experiment 1.—I excited the secretion of gastric juice by giving to one of the dogs some oxen's windpipe, boiled, but quite hard. The last quantities of gastric juice extracted were not mixed with the first; the first quantity, filtered, gave two ounces and four drachms, the second quantity six drachms, to which one drachm of the first quantity was added, in order to procure enough for the saccharimeter. The first quantity showed 32° rotation to the left, the second quantity showed 40°. It appeared, therefore, that the wind-pipe used for causing the secretion had been partly digested, and transformed into polarizing peptone; for if the optical properties of the fluid had been due to any other food which had remained in the dog's stomach since it had been last fed (although it was fasting at the time of the experiment), instead of having an increase of deviation from 32° to 40°, we should rather have expected a decrease of the rotating power.

Experiment 2.—The first and second quantities of gastric juice extracted in the preceding experiments were mixed together, the fluid showing 32°. (It ought to have been 34·5°. I cannot account for the discrepancy.) I took two quantities of the secretion, each measuring 1½ ounce, and placed them in two bottles of the same size; to one quantity I added 20 grammes of boiled wind-pipe cut up into small pieces, and both bottles were exposed for one hour to a temperature of 40° Centigrade, during which time the fluid containing the wind-pipe was frequently stirred. After an hour the mixture was filtered, when it appeared to me that the cartilaginous fragments had been partly dissolved, the edges having become somewhat rounded and worn off. The next day the filtrate was examined in the saccharimeter, when its action was found to be so powerful that the instrument was no longer available. In order to obviate this difficulty, I measured off 11 cubic centimetres of the gastric juice, and diluted it with an equal volume of distilled water. The diluted fluid was introduced into the tube of the instrument, and examined, when it showed 33° rotation. From this experiment, it is obvious that 1½ ounce of gastric juice, showing 32° rotation, after digesting 20 grammes of boiled oxen's trachea for one hour at a temperature of 40°, exhibited 66° rotation; its optical power had, therefore, increased to more than double; the polarizing peptone, which had been originally 3 per cent., being, consequently, at the conclusion of the experiment, 6·3 per cent. of the gastric juice. The other sample of gastric juice, which had been used for the sake of comparison, showed 31° at the close of the experiment; the difference of 1° is so small, that it need not be taken into consideration.

Experiment 3.—One of the dogs, after fasting for forty-two hours, was allowed to eat fragments of hard bone cut up and perfectly free from flesh. A first supply of about two ounces of gastric juice was obtained under the influence of these hard bodies, and this was thrown on a filter. I then gave the dog some more pieces of bone, but these contained pieces of cartilage adhering to them, or were partly cartilaginous. The animal ate these greedily, and I obtained a second quantity of the gastric fluid, more abundant than the first; this was filtered separately, and yielded a fluid nearly as colourless as water. The next day I examined both samples of gastric juice in Soleil's polariscope. That obtained by the first process, *i.e.* after giving the animal bones free from flesh and cartilage, showed between 6° and 7° rotation; the samples extracted after the dog had eaten the bones and cartilage, showed between 17° and 18° rotation; it is, consequently, evident that the cartilaginous part of the bones had undergone digestion, and had increased, or greatly contributed to increase, the quantity of polarizing peptone from 0·6 per cent. to 1·6 per cent. of the gastric juice.

Finally, I may state that the residue of gastric juice obtained with wind-pipe or soft bones, contains a very large percentage of polarizing peptone. In one instance, where the indication in Soleil's polariscope was 31°, the proportion of the substance amounted to no less than 78 per cent. of the dry residue; and in another instance, where the gastric juice showed only 7° rotation, the proportion of this substance amounted to 32 per cent. of the dry residue. In these determinations a known weight of gastric juice was neutralized with a normal solution of potash, and then evaporated to dryness; the weight of the potash added was afterwards subtracted from that of the dry residue.

I have so far assumed that there is no other substance in gastric juice which rotates the plane of polarization of light; indeed, this appears to me satisfactorily shown by the investigations related in the present communication.

The following results are derived from my researches on the constituents of gastric juice.

1. That gastric juice, when its secretion is excited by means of soft (cartilaginous) bones, or the substance of wind-pipes, is invariably possessed of the property of rotating more or less the plane of polarization of light to the left.

2. That this optical property of gastric juice is due to its containing a substance exhibiting the chemical properties of Lehmann's *peptone,* a product of digestion; and 0·024 grammes of the substance, or a weight closely approximating to this, dissolved in 25 c.c. of water, rotates the plane of polarization 1° in Soleil's saccharimeter.

3. That gastric juice, when obtained after washing out the animal's stomach with water, and exciting its secretion by means of non-digestible bodies, such as silicious pebbles, exerts no action whatever on polarized light, thereby confirming the second conclusion.

4. That there is every reason to believe the above substance to be the only constituent of gastric juice possessed of the property of acting on polarized light.

5. That the substance to which gastric juice owes its optical properties is a product of digestion of the wind-pipes, or of the soft or cartilaginous bones used for exciting its secretion.

XXI.—*On the Peroxides of Potassium and Sodium.*

By A. Vernon Harcourt, Esq., F.C.S.
(STUDENT OF CHRISTCHURCH.)

In 1810, three years after the discovery of the metals of the alkalies, the products of their oxidation were investigated by MM. Gay-Lussac and Thénard in France, and by Sir Humphry Davy in this country. These metals could then be obtained only in very small quantity. Sir H. Davy seems to have used in his experiments from one to eight grains, and MM. Gay-Lussac and Thénard employed a measured quantity which weighed no more than $\frac{3}{10}$ths of a grain. Another source of error in both sets of experiments was that the oxidation, instead of being allowed to proceed slowly, was suddenly effected at a high temperature by burning the metals in air or oxygen. It is probably to these two causes that we must attribute the fact that these distinguished chemists failed to ascertain the constitution of the alkaline peroxides.

MM. Gay-Lussac and Thénard* give a table of the numbers which they obtained by burning a known weight of potassium in oxygen, and measuring the volume of gas absorbed. These numbers are in truth singularly discordant, and the authors draw from them no other conclusion than that "the potassium had combined with twice and even three times as much oxygen as it requires to pass into the state of potash." In three experiments they weighed the oxide formed, in order to prove that "whatever is the quantity of oxygen which potassium absorbs, the weight of the oxide is always equal to that of the potassium employed and of the oxygen absorbed, and therefore no volatile product is disengaged." In these three experiments, however, the weight of oxide formed, compared with that of the potassium employed, agrees with the supposition that this body is a teroxide. But it is plain from the expressions above quoted that the authors did not regard them as decisive of this point. With reference to the peroxide of sodium, they state similarly, as the result of their experiments, that "sodium can take up half as much oxygen again as it requires to pass into the state of soda, and even more." Sir H. Davy referring to this research says,† "I have been able to confirm in a general way these interesting results, though I have not found any means of ascertaining accurately the quantity of oxygen contained in these new oxides."

These extracts are sufficient to show that the definite statements as to the constitution of these bodies, which have found their way into most works on chemistry, and which are at variance with my conclusions, cannot rightly claim the authority of the great names which they allege.

The experiments of which I am about to give an account originated some time ago in the investigation of the action of carbonic oxide upon potassium made by Professor Brodie, under whose directions the earlier and more critical of them were performed. They have been conducted throughout in the laboratory of the University of Oxford.

The primary experiment consists in submitting a known weight of potassium or sodium to the regulated action of oxygen gas. It is necessary for this purpose that the metal should be pure, and have as clean a surface as possible; both that it may be accurately weighed, and because a crust of hydrate hinders the action of the gas. As its preparation in this condition requires some little care, and is thus essential to the success of the operation, it may not be out of place to describe the means by which it has been effected.

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* Recherches Physico-chimiques, Tome i., p. 132.

† Bakerian Lecture, 1810.

The potassium or sodium was first purified, shortly before being used, by filtration through linen. The arrangement finally adopted for this purpose consists of two tubes, of which the outer is a large and stout test-tube, about eight inches long and rather more than an inch in diameter; the inner is of the same length but one-third narrower, and open at both ends. Over one end of the inner tube, which is bent outwards into a lip, a piece of linen is tightly bound. This smaller tube should reach to within about an inch and a-half from the bottom of the larger, and it is secured in this position by passing through a cork which fits loosely into the outer tube. For a piston, I employ a cylindrical cork, which will pass, by gentle pressure, from end to end of the inner tube, and a stout glass rod for piston-rod. A small hole pierced in the cork permits the air to escape when the piston is being forced down, but does not allow the passage of the melted metal. When the apparatus is thus complete, it is half filled with naphtha, and the globules of potassium (or sodium, as the case may be,) are introduced into the inner tube. Ten or twelve grammes may conveniently be filtered at one operation in tubes of the size described. The temperature is carefully raised until the potassium fuses; the cork is then introduced and pressed gradually down upon the melted metal, which passes in a fine shower through the linen strainer to the bottom of the outer tube, and is perfectly freed from its coating of oxide. When the whole has cooled, the inner tube is removed, and the small metallic particles may be aggregated into globules of a convenient size by being again fused and judiciously stirred and pressed with a glass rod. In order to free from naphtha and introduce into the bulb, in which it is to be subjected to the action of the gas, a sufficient quantity of potassium at one operation, a number of these smaller globules, are cast into a cylinder. I employ for this purpose a glass tube, of about half an inch in diameter, and three inches and a-half in length, which has been closed at one end like a test-tube and then divided by a crack lengthwise, from end to end. The two halves are re-united for the operation by being bound round with thread, and the mould thus formed is placed in a wider but rather shorter test-tube. It is then two-thirds filled with naphtha, which passes also into the outer tube, and the clean globules of potassium are rapidly introduced; by applying heat and stirring with a thin glass rod, the globules are readily united into one. In this way a solid cylinder of potassium is obtained, between one and one and a-half inch in length, and weighing from two to three grammes, which crystallizes on cooling with a brilliant metallic surface.

The apparatus used in the actual oxidation of the metal consists of a gas-holder of air and a gas-holder of oxygen; a washing bottle, containing solution of caustic potash, with which, by means of two separate tubes dipping into the fluid, both gas-holders communicate; a Liebig's bulb-apparatus, filled with the same solution; two U-tubes, containing respectively fragments of caustic potash, and pumice impregnated with strong sulphuric acid; a bulb of hard glass, in which the metal is exposed to the action of the gas; an air-bath for maintaining the bulb and its contents at a uniform temperature; and, lastly, a bulb-tube containing sulphuric acid, through which the gas passes as it issues from the apparatus. This bulb-tube (fig. 1) serves to close the apparatus against diffusion, to mark the rate of passage and pressure of the gas, and to dry any bubbles of air which a too rapid absorption may draw back into the bulb. The capacity of the bulb itself (fig. 2) is about 150 c. c. It is provided with an india-rubber cork, through which two small tubes, bent at a right

Fig. 1.

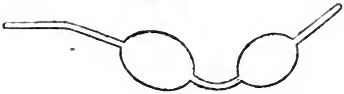
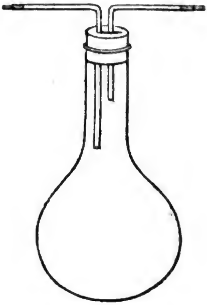


Fig. 2.



angle, pass into its interior. These, when gas is to be transmitted, are connected by pieces of caoutchouc tubing, one with the drying apparatus, and the other with the bulb-tube. They are closed when the bulb is removed from the apparatus with plugs of india-rubber.

The first operation is to dry the bulb absolutely by connecting it with the apparatus, and heating it while a current of air is passed through. When cool it is again disconnected, closed by replacing the plugs in the delivery-tubes, and weighed. It is next filled with dry nitrogen, and again weighed. Meanwhile the split-tube in which the metal has been cast is transferred to a dish containing naphtha of a low boiling point, and the thread, with which it is bound together, is removed; the solid cylinder is readily detached on opening the mould, and may be washed for a moment in the fresh naphtha. It is then rapidly transferred, still covered with naphtha, to a tube through which a current of dry nitrogen is being passed; and the tube is immediately closed by a cork holding a piece of small tubing drawn out to a fine point. By the application of a gentle heat, the naphtha may be completely distilled off in the current of nitrogen. When this is effected, and the bulb is in readiness, the two corks are removed simultaneously, and the mouth of the bulb applied to the end of the tube; by depressing this end the cylinder of potassium is caused to glide, protected by the nitrogen, from one into the other. The cork with its glass tubes is replaced and the bulb and potassium weighed. I have never succeeded in bringing the metal into the bulb with its lustre unimpaired, owing, probably, to the presence of a trace of oxygen in the nitrogen used; but the undiminished sharpness of the lines of crystallization on the surface, and the dull metallic appearance which it still retains, seem to show that the superficial oxidation is quite insignificant. When the surface of the metal is dried with blotting-paper, an opaque white crust is formed, and a little naphtha always remains behind, however rapidly and carefully the operation is performed. The bulb is now placed in an air-bath, and re-connected with the drying apparatus before described; heat is applied, and when the metal is in a state of fusion, air is very slowly passed through. The point at which the action commences has varied in different experiments. With potassium it is generally rather above 100° C., and with sodium, about 200° C. In both cases, when the action is once set up, it will continue at a much lower temperature, down apparently to the point of solidification of the metal.

The phenomena of the oxidation of potassium are remarkable.* Soon after the dry air has begun to mix with the nitrogen in the bulb, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single, spluttering spark appears at one point and a dust of white oxide rises in the bulb. At this instant the absorption begins. If very little oxygen is present in the bulb, the action is perfectly manageable, and the quantity of white oxide floating about is insignificant. But if the nitrogen has been replaced by air too quickly, a rapid absorption takes place, until the degree of dilution requisite for a gradual action has been attained, and a cloud of oxide covers the inner surface of the bulb, and passes, with each bubble of gas, through the sulphuric acid out of the apparatus. If, to obviate this, a plug of asbestos is placed in the exit tube, it becomes choked, and the transmission of gas is no longer possible. At the point at which the spark makes its appearance, the blue crust becomes white, and this change passes in a moment over its whole extent. Immediately afterwards it disappears entirely beneath the liquid metal, whose smooth surface is soon broken by innumerable projections which ascend and ramify with a steady, visible growth, having the white lustre of frosted silver. At the same time the metal climbs rapidly up the surface of the glass, extending in broad foliations, which grow together from side to side and cover sometimes the whole of the interior of the bulb. In more than one instance, the experiment has been abruptly terminated by this exuberant growth having reached to the delivery-tubes and stopped the passage of the gas. This phenomenon is probably due to the rising of the liquid metal by capillary attraction through the bulky powder which is being constantly formed upon its surface. At each point to which it thus ascends, it is converted into fresh oxide, which is flooded in its turn by fresh metal. After two or three hours, according to the rate at which air has been introduced, the whole becomes solid and the growth ceases. Gradually, as the oxidation proceeds, the metallic coating of the inner surface of the bulb changes to a dead white, and the brilliant undergrowth crumbles down into a shapeless powder.

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* The changes which take place may conveniently be observed by using a beaker for air-bath during the first stages of the action.

No one who has watched these changes can doubt that the action consists of at least two stages. By carefully regulating the heat and the supply of air, nearly the whole of the potassium may be converted into a white oxide. I have endeavoured, by discontinuing the action and weighing the bulb and its contents, to determine exactly the amount of oxygen which had been absorbed when this point was reached. But, in every case, before the dark metallic foliations had quite disappeared, some portions of the oxide had assumed the yellow colour characteristic of the final product. Two weighings made at this point render it probable that the white oxide is a binoxide; but I have never yet terminated the action at this stage and made an analysis of the product, because of the evident want of homogeneity above mentioned. Finally the temperature is raised, and oxygen transmitted in the place of air. Even at this point, the operation may be ruined by a too speedy admission of the pure gas; for great heat is produced by the rapid absorption thus set up, sufficient even to melt the oxide which has been formed; the glass is attacked, and the fused mass, having become impervious to the gas, is incapable of complete oxidation. The safest course is to employ air until nearly the whole is converted into yellow oxide.

The action is brought to a close only with difficulty, or at least after a long time. I give one example: -The weight of potassium in the experiment was 1·608 gms. The first weighing was made when the conversion into yellow oxide appeared to be effected.

Weight of bulb and oxide				29·2624
Do. after the passage of oxygen for	8 hrs. at		210° C.	29·2924
,, ,,	4	,,	280°	29·3497
,, ,,	8	,,	230°	29·3645
,, ,,	4	,,	230°	29·3658
,, ,,	8	,,	230°—280°	29·3725
,, ,,	4	,,	270°—280°	29·373

The final product is a powder of the colour of chrome yellow. It cakes together when subjected for some hours to a temperature of 280° C., but may in great part be broken up within the bulb, and separated from the sides by gentle tapping and shaking. When exposed to the air, it rapidly absorbs moisture and gives off oxygen. It effervesces strongly on being thrown into water. It contains four atoms of oxygen, and is represented by the formula K_2O_4.* The action of water upon it consists in the formation of two atoms of oxygen gas and one atom of binoxide of potassium, thus :—

$$K_2O_4 = K_2O_2 + O_2$$

I have ascertained the constitution of this body by determining, (1) the potassium which it contains, (2) the oxygen evolved from it by the contact of water and platinum black, (3) the oxygen evolved by the contact of water alone, and (4) the oxygen remaining in form of binoxide in the aqueous solution.

1.—*a.* 2·7665 grms. of potassium yielded 4·925 grms. of peroxide.

b. 1·6079 grms. potassium yielded 2·8779 grms. peroxide.

c. ·2946 grm. peroxide gave ·3648 grm. sulphate of potassium.

d. ·2276 grm. peroxide gave ·2765 grm. sulphate of potassium.

e. ·4495 grm. peroxide gave ·4481 grm. sulphate of potassium.

f. ·1414 grm. peroxide required for neutralization 7·07 c. c. of a standard solution of sulphuric acid, of which 1 c. c., according to a determination with chloride of barium, corresponded to ·01115 grm. potassium.

g. ·5093 grm. peroxide required 49·26 c. c. of a sulphuric acid solution, of which 1 c. c. corresponds to ·005682 grm. potassium.

2.—*a.* ·5844 grm. peroxide was introduced into a small apparatus contrived by Professor Brodie, consisting of a flask, in which the weighed amount of oxide is placed, together with, in these experiments, a small quantity of platinum-black,—a stoppered bulb, containing the fluid which is to be brought into contact with the oxide, and a potash-tube to dry the escaping gas. By loosening the stopper of the bulb, the water is suffered to descend upon the peroxide; a violent effervescence ensues. Five or ten minutes are generally sufficient to complete the action. The loss of oxygen in this experiment amounted to ·1894 grm.

b. ·584 grm. peroxide, treated in the same way, lost ·1825 grm. oxygen.

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* O = 16; S = 32; C = 12.

3.—These experiments were made in exactly the same way as the last two, except that no platinum-black was placed in the flask.

a. ·4495 grm. peroxide lost ·0906 grm. oxygen.
b. ·2927 grm. peroxide lost ·0624 grm. oxygen.
c. ·5184 grm. peroxide lost ·124 grm. oxygen.
d. ·5291 grm. peroxide lost ·1098 grm. oxygen.

In *a*, the flask was immersed in a freezing mixture during the decomposition. In *b*, the water used was acidulated with sulphuric acid. Both methods were successful in preventing the decomposition of the solution of binoxide which is formed. In *c*, neither precaution was taken, and bubbles continued to rise through the fluid after the termination of the first action. The number representing the loss of oxygen is for this reason too high, and the binoxide remaining in the liquid, determined immediately afterwards with permanganate solution, was proportionately too low.

4.—*a.* ·2954 grm. peroxide, dissolved in water acidified with sulphuric acid, decolorized 54·39 c. c. of a solution of permanganate of potassium,* of which 1 c. c. corresponded to ·000595 grm. oxygen.

b. ·2049 grm. peroxide thrown into water containing ice, effervesced equally on the first contact, and decolorized 37·53 c. c. of the same standard solution of permanganate.

c. ·0899 grm. peroxide similarly treated, required 16·27 c. c. of permanganate.

d. ·0595 grm. peroxide required 10·8 c. c.

e. ·0614 grm. peroxide required 11·1 c. c. of a permanganate solution, of which 1 c. c. corresponded to ·000616 grm. oxygen.

These numbers, calculated on a hundred parts of the peroxide used, are compared below with those deduced from the atomic weight assigned to it.

		At. W.	p. c.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
1.	K_2	78	54·93	56·17	55·87	55·51	54·45	55·86	55 ·8	54·96
	O_4	64	45·07							
	K_2O_4	142	100·00							

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* This reaction has been ascertained by Professor Brodie to be perfectly definite, the two solutions losing exactly equal quantities of oxygen.

		At. W.	p. c.	a.	b.
2.	K_2O	94	66·2		
	O_3	48	33·8	32·41	31·25
	K_2O_4	142	100·0		

				a.	b.	c.	d.
3.	K_2O_2	110	77·46				
	O_2	32	22·54	20·19	21·3	23·9	20·75
	K_2O_4	142	100·00				

				a.	b.	c.	d.	e.
4.	K_2O_3	126	88·73					
	O	16	11·27	10·95	10·9	10·77	10·98	11·14
	K_2O_4	142	100·00					

I am sensible that numbers might be obtained, agreeing more closely than some of these do with the calculated results; but—regarding especially the ratio of the weights of oxygen in the three sets of determinations,—these seem to me already sufficient to leave no doubt as to the constitution of this peroxide.

The phenomena of the oxidation of sodium resemble, in some degree, those already described as occurring in the case of potassium. But they are far less striking. The growth upon the surface of the fused metal, in the first stage of oxidation, is lower and less tree-like; its lustre is soon dulled by a covering of white oxide. The metal does not spread itself on the glass, and in consequence a larger quantity may be operated upon at once in a bulb of the same size. I have several times employed Florence flasks for the oxidation of sodium; but they are always attacked to some extent by the oxide, which has more action upon glass than the peroxide of potassium at the same temperature. A shorter time and a rather lower temperature is required for the complete peroxidation of sodium than of potassium. The peroxide of sodium is of a pure white colour; like the oxides of zinc and tin, it becomes yellow when heated, and on cooling again loses this tint. Exposed to the air, it slowly deliquesces, and after a while resolidifies as carbonate. Great heat is produced on mixing it with water, and a small quantity of gas is evolved;* the quantity is least when the peroxide is in the state of fine powder, and is projected little by little into a large excess of acidulated water. If a small heap of it is moistened, it becomes yellow with heat, and the disengagement of gas is considerable. It contains two atoms of oxygen, and is represented by the formula Na_2O_2. The normal action of water upon it consists in the simple solution of the binoxide.

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* This evolution of gas probably results from the local heating of the moistened peroxide: for the concentrated alkaline solution is rapidly decomposed at the boiling point.

I have determined, in order to ascertain its constitution, (1) the sodium which it contains, and (2) the weight of oxygen which it loses by the contact of water and platinum-black, or when reduced by a standard solution of permanganate of potassium.

1.—*a.* 2·5225 grms. sodium yielded 4·2443 grms. peroxide.
b. 3·6418 grms. sodium yielded 6·1233 grms. peroxide.
c. 11·8085 grms. sodium yielded 19·79 grms. peroxide.
d. ·2861 grm. peroxide gave ·522 grm. sulphate of sodium.
e. ·4461 grm. peroxide gave ·8075 grm. sulphate of sodium.
f. ·3118 grm. peroxide required for neutralisation 28·1 c. c. of a standard solution of sulphuric acid, of which 1 c. c. corresponds to ·00658 grm. sodium.
g. ·352 grm. peroxide required 61·7 c. c. of sulphuric acid, of which 1 c. c. corresponds to ·003358 grm. sodium.
h. ·4132 grm. peroxide required 72·6 c. c. of the same acid.

2.—*a.* ·0979 grm. peroxide required, to impart colour to its solution, 31·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·00063 grm. oxygen.
b. ·1124 grm. peroxide required 42·75 c. c. of a solution of which 1 c. c. corresponded to ·000516 grm. oxygen.
c. ·0327 grm. peroxide required 8·4 c. c. of a solution of which 1 c. c. corresponded to ·000774 grm. oxygen.
d. ·1302 grm. peroxide required 33·46 c. c. of the same solution.
e. ·0715 grm. peroxide required 18·33 c. c. of the same.

The results per cent., derived from these numbers, are exhibited below :—

				a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
1.	Na_2	46	58·97	59·43	59·47	59·6	59·1	58·64	59·28	58·86	59
	O_2	32	41·03								
	Na_2O_2	78	100·00								

				a.	*b.*	*c.*	*d.*	*e.*
2.	Na_2O	62	79·49					
	O	16	20·51	20·33	19·64	19·88	19·89	19·84
	Na_2O_2	78	100·00					

Several experiments were made in the flask-and-bulb apparatus, before described, of the action upon the binoxide of water and platinum-black. The numbers arrived at agreed perfectly with those obtained in the determinations with permanganate of potassium.

When a solution of this binoxide of sodium is evaporated on a water-bath, oxygen is given off, slowly at first, but rapidly when the solid residue is beginning to separate. But if the evaporation is allowed to proceed slowly, at ordinary temperatures, by placing the solution under a bell-jar over sulphuric acid, large tabular crystals, of a hexagonal form, make their appearance.

These crystals are a hydrate of the binoxide of sodium. Their constitution was determined in the following manner:

When nearly the whole of the water had evaporated, the crystals were spread rapidly between two thick folds of blotting paper, round which a sheet of india-rubber was wrapped to prevent the access of carbonic acid. The whole was then strongly pressed for eight or ten hours.

In two preparations, the crystals thus dried were at once divided into two portions and analysed. One portion was dissolved in dilute acid, and the oxygen contained in it determined by a standard solution of permanganate of potassium. The other was placed in a silver boat and heated in a current of dry carbonic acid, by which the binoxide is readily converted into simple carbonate; the water which separates was collected at the same time in a weighed drying-tube. The increase in weight of this tube and the weight of the carbonate which has been formed, indicate at once the amount of water and of sodium which the hydrate contains. The following are numbers obtained in these analyses; they show that the crystallized hydrate consists of a combination of one atom of the anhydrous binoxide with eight atoms of water.

Preparation 1.—*a.* ·2546 gm. of crystallized hydrate required 29·72 c.c. of permanganate solution,* of which 1 c.c. yielded ·0006116 grm. oxygen.

b. ·3968 grm. of hydrate gave ·1912 grm. carbonate of sodium, and ·2527 grm. water.

Preparation 2.—*a.* ·2350 grm. of hydrate required 26·82 c.c. of the same permanganate solution.

b. ·3614 grm. of hydrate gave ·176 grm. carbonate of sodium, and ·2305 grm. of water.

To place it beyond a doubt that the residue in these experiments consisted purely and simply of carbonate of sodium, it was washed into a flask, coloured with litmus, and determined by means of a standard acid solution. The results obtained were conclusive,—*e. g.*, ·176 grm.,—the weight of carbonate obtained in the last experiment,—required 22·72 c. c. of an acid solution, of which 1 c. c. corresponded to ·003358 grm. of sodium. This weight of pure carbonate of sodium ought theoretically to have required 22·74 c. c. of such a solution.

The percentage composition of this hydrate calculated from the foregoing data is compared below with that deduced from the formula assigned to it; the oxygen actually found being half that which the binoxide contains, its number is doubled:—

			Prep. 1.	Prep. 2.
Na_2	46	20·72	20·91	21·10
O_2	32	14·42	14·28	13·96
$8H_2O$	144	64·86	63·68	63·78
$Na_2O_2,8H_2O$	222	100·00	98·87	98·84

In a third preparation of the hydrate, the quantity of water which it loses when left to effloresce over sulphuric acid, was determined. The crystals, after having been dried as before, and weighed between watch-glasses, were exposed under a bell-jar over sulphuric acid, and re-weighed at intervals of two or three days. After nine days the weighings became constant, and the residue was determined as in the preceding experiments.

a. ·647 grm. of crystallized hydrate yielded ·3287 grm. of effloresced hydrate, and lost consequently ·3183 grm. of water.

b. ·2226 grm. of effloresced hydrate, heated in a current of dry carbonic acid, yielded ·2071 grm. of carbonate of sodium. The water given off weighed ·071 grm.

c. ·0268 grm. of effloresced hydrate, dissolved in acidified water, decolorized 5·98 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

The weight of water lost by the crystallized hydrate in Exp. *a*, corresponds to six out of the eight atoms which it contains. The residue must therefore have the constitution Na_2O_2, $2H_2O$. Determinations *b* and *c* confirm this conclusion.

		Theory.		Found.
a.	$Na_2O_3,2H_2O$	114	51·35	
	$6H_2O$	108	48·65	49·2
	$Na_2O_2,8H_2O$	222	100·00	
b.	Na_2	46	40·35	40·37
	O_2	32	28·06	
	$2H_2O$	36	31·59	31·89
	Na_2O_2, $2H_2O$	114	100·00	
c.	Na_2O	62	54·38	
	O	16	14·03	13·65
	$2H_2O$	36	31·59	
	Na_2O_2, $2H_2O$	114	100.00	

It is worthy of remark that this hydrate stands in the same relation to a sesquihydrate and a protohydrate in which the binoxide stands to a sesquioxide and a protoxide. For if we subtract the formula of a protoxide from that of a sesquioxide, we obtain the formula of a binoxide; and similarly, by subtracting the formula of a protohydrate from that of a sesquihydrate, we obtain the formula of the hydrate of this binoxide :—

$$\begin{array}{lll}
M_4O_3 & M_2H_3O_3 & = \tfrac{1}{2}\,(M_4O_3 + 3H_2O) \\
M_2O & M\ H\ O & = \tfrac{1}{2}\,(M_2O + H_2O) \\
\hline
M_2O_2 & M\ H_2O_2 & = \tfrac{1}{2}\,(M_2O_2 + 2H_2O)
\end{array}$$

Or again, as we compare a sesquioxide and the hydrate corresponding with a protoxide and its hydrate by the assumption of a distinct atomic weight, writing *e. g.* fe_2O, and $feHO$ where $fe = \frac{2}{3}\ Fe$, so the binoxide with its hydrate may, for the sake of a similar comparison, be represented by the formulæ na_2O and $naHO$, where $na = \frac{1}{2}\ Na$.

The formation of these hydrates, together with the fact of the increased stability of a solution of peroxide when acidified, suggested the expectation that corresponding salts might be obtained. Accordingly, three portions of a solution of binoxide of sodium were exactly neutralized with sulphuric, nitric, and hydrochloric acids respectively, and evaporated to dryness by exposure over sulphuric acid. The crystals which were formed consisted simply of sulphate, nitrate, and chloride of sodium. This experiment was repeated with the same result.

It has been stated that when the tetroxide of potassium is projected into water, a solution of binoxide is formed. It seemed probable that, by the slow evaporation of this solution, a hydrate might be obtained corresponding to the hydrate of the binoxide of sodium. Such, however, is not the case. Upon reaching a certain degree of concentration, the solution is entirely decomposed, with evolution of oxygen. The ultimate residue is opaque and slightly crystalline. It contains no binoxide.

The behaviour of these peroxides with various chemical reagents offers an interesting subject for investigation. I have already made a few experiments of this kind, a brief account of which I may be allowed here to append.

The general form of these experiments has been the same. The peroxide was placed in a boat of glass, silver, or platinum, and weighed in a small test-tube. The boat, with its contents, was then transferred to a piece of combustion-tubing connected at one end with an apparatus for drying the gas to be transmitted, and at the other with a bulb-tube (fig. 1) containing sulphuric acid. Heat was applied, as seemed requisite, by means of a lamp placed beneath the tube. When the action appeared to be complete, the boat and its contents were withdrawn, replaced in the test-tube, and again weighed. The operation was repeated a second time, or several times if necessary, until two successive weighings gave nearly the same result.

The first of these experiments consisted in heating the peroxides in an atmosphere of nitrogen, in order simply to ascertain their behaviour at a high temperature. 0·2288 grm. of binoxide of sodium were exposed in a silver boat to the strongest heat of a large Argand gas-burner. The powder passed from white to a full yellow, and caked together, but neither fused nor decomposed. The flame from a wire-gauze gas-burner, playing round the glass tube which contained the boat, produced partial fusion; at the same time, the silver was strongly acted upon, but no oxygen was evolved. The temperature was then allowed to fall. The colour of the fused mass was black while hot, brown on cooling. It weighed ·2244 grm. On treating it with water, a quantity of oxide of silver separated, which was at the same moment reduced, with effervescence, by the excess of unaltered binoxide of sodium. Hence the only reaction which can be thus observed is that of the binoxide upon the silver: $Na_2O_2 + Ag_2 = Na_2O + Ag_2O$.

The tetroxide of potassium, similarly heated, became first of a deep orange colour, and then melted to a black fluid, which, when the temperature was allowed to fall, crystallized with shining tabular surfaces; the whole, on further cooling, gradually became yellow again. Its weight after it had been thus fused was unaltered. On applying the full heat of a large gas flame the black fluid was gradually decomposed with evolution of oxygen; the residue became grey and infusible. The loss of weight corresponded to a loss of two atoms of oxygen.

·504 grm. of tetroxide of potassium left a residue weighing ·3933 grm., or 78·4 per cent. If 2 atoms of oxygen are evolved, the proportion of the residue should be 77·47 per cent.

The weight of silver acted upon was ·597 grm., or rather more than 1½ atom for 1 atom of peroxide. The action, whose completion the infusibility of the residue may have hindered, is doubtless the following:

$$K_2O_4 + Ag_2 = K_2O + Ag_2O + O_2.$$

From the fact that 2 atoms of oxygen were evolved while less than 2 atoms of silver were acted upon, it would seem to follow that the former action occurs independently of the latter.

Several attempts have been made, by bringing together sulphur and the tetroxide of potassium, to obtain the reaction,

$$K_2O_4 + S = K_2SO_4.$$

When these two bodies are heated together, a violent deflagration takes place; but by distilling the vapour of sulphur over the peroxide in an atmosphere of nitrogen, the action may be made to proceed gradually. In all the experiments, some sulphate was formed, and in one a large proportion; but, unless the temperature and the supply of sulphur vapour are most carefully regulated, the principal products are a polysulphide, of liver-colour, and sulphurous acid. Binoxide of sodium also readily combines with sulphur vapour, forming a brown fusible mass which contains a polysulphide and a little sulphate. Sulphurous acid is disengaged.

When binoxide of sodium is similarly heated in the vapour of iodine, the two gradually combine. The product is a white fusible body, apparently quite homogeneous.

·203 grm. of binoxide of sodium yielded ·8181 grm. of this substance; whence the amount of product corresponding to 100 parts of the binoxide is 403 parts.

According to the equation,

$$Na_2O_2 + I_2 = Na_2OI_2 + O;$$

100 parts should yield 405 parts. This equation represents in the simplest form the change of weight that has taken place, the substitution for an atom of oxygen of the equivalent quantity of iodine; but the residue may also consist of a mixture of iodide of sodium with iodite of sodium or iodate, *e. g.*:

$$3Na_2O_2 + 3I_2 = 5NaI + NaIO_3 + 3O.$$

On dissolving the product and adding an acid, a copious precipitate of iodine was formed. This iodine was determined, and the quantity found agreed with the conclusion above stated.

Action of Carbonic Oxide upon Binoxide of Sodium.

The dry gas, in this and the succeeding experiments, was slowly led through the tube in which the boat with its contents was placed, and the current from time to time discontinued; any absorption or evolution of gas could thus be readily noted by watching the movements of the fluid in the sulphuric acid bulb-tube (Fig. 1). At a temperature of 100°—150° C., a slight absorption took place. On raising the heat, it proceeded rapidly, a dark shade passing over the surface of the binoxide, which was at the same time partially fused. After a while, it again proceeded slowly, and the contents of the boat became once more white.

The weight of binoxide of sodium taken was ·352 grm.: the weight of the product ·4753 grm.; being in the ratio of 100 : 135.

According to the equation,

$$Na_2\,O_2 + CO = Na_2\,CO_3,$$

100 parts of binoxide of sodium should yield 135·9 parts of carbonate. The product was also identified qualitatively.

Action of Carbonic Acid upon Binoxide of Sodium.

At a temperature below 100° C. the first sign of action appeared. A shade of brown, as in the preceding experiment, passed over the binoxide, and at the same moment a slight absorption took place. On raising the temperature, after an hour's slow passage of the gas, a similar further action ensued. Finally the residue was perfectly white.

The weight of binoxide of sodium taken was ·4132 grm. that of the product ·5565 grm., being in the ratio of 100 : 134·7.

The product is, therefore, as before, carbonate of sodium; and the reaction which takes place is the following:

$$Na_2\,O_2 + CO_2 = Na_2\,CO_3 + O.$$

Action of Carbonic Oxide upon Tetroxide of Potassium.

The action was set up at a temperature of rather more than 100° C.; a single scintillation and a deepening of the colour of the peroxide marked its commencement. A weighed Liebig's potash-bulb apparatus and potash-tube had been attached to the apparatus, in order to determine the carbonic acid which it seemed probable might be formed. The even passage of the gas through the bulbs, while its action upon the peroxide was proceeding rapidly, showed that its volume suffered neither diminution nor increase. The residue in the boat, when the action was completed, was white. ·2314 grm. of tetroxide of potassium yielded ·2245 grm. of this product, numbers in the ratio of 100: 97. 100 parts of the tetroxide should yield, theoretically, 97·2 parts of carbonate of potassium. The product was also identified qualitatively.

The potash-bulbs and tube gained only ·005 grm. In another experiment, where the gas issuing from the apparatus was passed through lime-water, no turbidity whatever was produced.

The reaction is, therefore, that expressed by the following equation:

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

The perfect constancy in the volume of the gas throughout the experiment goes to prove, not only that the volume of oxygen evolved is equal to that of the carbonic oxide absorbed, but that the two actions proceed proportionally. The carbonic oxide is substituted for an equivalent quantity of oxygen,

$$K_2O_2,O_2 + CO = K_2O_2,CO + O_2.$$

Action of Carbonic Acid upon Tetroxide of Potassium.

In the cold apparently no action took place, but it was set up below 100° C. The contents of the boat changed colour gradually from yellow to white. A quantity of oxygen was evolved. ·4498 grm. of the tetroxide yielded a product which weighed ·4379 grm. These numbers are in the ratio of 100 : 97·35. The product consisted of carbonate of potassium. The reaction is represented by the equation,

$$K_2O_4 + CO_2 = K_2CO_3 + O_3.$$

Action of Protoxide of Nitrogen upon Binoxide of Sodium.

The gas employed was prepared in the usual manner from nitrate of ammonium, washed with solutions of sulphate of iron and of caustic potash, and carefully dried. It had no action upon the binoxide until a temperature had been reached at which the latter showed signs of fusion, and of attacking the silver boat. At this point, a few particles became suddenly of a deep red, and this change passed by degrees upon the whole mass, which, though the heat was lowered, fused gradually with effervescence. A slight absorption took place, and the issuing gas lost for a while its power of brightening a glowing splinter of wood. The product was examined qualitatively. It had an alkaline reaction and gave off nitrous fumes in great abundance upon the addition of sulphuric acid.

A little of the substance had been thrown, by the effervescence which followed its fusion, out of the silver boat upon the sides of the glass tube in which it was placed. These spirtings were washed out, after the close of the experiment, and converted into chloride. The chloride thus formed weighed ·0791 grm. The weight of binoxide of sodium originally taken was ·9068 grm.; which, after subtracting the weight of the amount lost, as deduced from the above determination, becomes ·8542 grm. The product, which was shown by the qualitative examination to consist principally of nitrite of sodium, weighed 1·4049 grm. These numbers are in the ratio of 100 : 164.

According to the reaction,

$$Na_2O_2 + 2N_2O = 2NO_2Na + N_2,$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite.

The alkaline reaction of the solution revealed one cause of the above deficiency, viz., the presence in the product of binoxide of sodium which had not been acted upon. The reaction might be due also to the presence of caustic alkali; but its formation under the above circumstances is exceedingly improbable, except through the action of the silver, and this action is insignificant in amount.

The phenomena of a second experiment exactly resembled those of the first; the absorption and the formation of nitrogen were well marked. There was again some loss by spirting, some action on the silver boat, and some alkali, presumably binoxide, remaining in the product. The error from these sources seemed more capable of being determined and thus eliminated, than of being avoided in any repetition of the experiment.

Accordingly, the spirtings were converted into sulphate and weighed; the amount of unchanged binoxide was determined by a standard acid solution; the silver boat was cleaned from oxide and its loss of weight ascertained; and, finally, the total amount of nitrite was determined by means of permanganate of potassium.

a. The sulphate formed from the spirtings weighed ·083 grm.

b. The solution of the total product required for its neutralization 10·4 c. c. of an acid solution, of which 1 c. c. corresponded to ·003376 grm. of sodium.

c. The same solution, largely diluted, and acidified, decolorized 305·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

d. The silver boat had lost by oxidation ·022 grm.

Hence we have,—

Weight of binoxide originally taken . . .		·6047 grm.
Deduct—*a.* For loss by spirting .	·0456 grm.	
b. For unchanged binoxide	·0595 grm.	
Total . .		·1051 grm.
Weight of binoxide which has taken part in the reaction		·4996 grm.
Weight of the total product		·9491 grm.
Deduct—*b.* For unchanged binoxide	·0595 grm.	
d. For oxidation of the silver boat . . .	·0016 grm.	
Total . .		·0611 grm.
Actual product of the reaction . .		·888 grm.

·4996 : ·888 :: 100 : 177·7

A ratio closely coinciding with that calculated from the equation already given.

If we suppose the small quantity of binoxide of sodium reduced to protoxide by the silver of the boat to have remained in that condition and not to have been reoxidized by the protoxide of nitrogen, the ratio becomes 100 : 178.

The amount of nitrite calculated from determination *c*, after making a correction for the admixture of binoxide,* is ·859 grm. The deficiency was due to insufficient dilution causing the escape of a little nitrous gas.

Nitrous oxide does not act upon tetroxide of potassium at any temperature to which the latter can be heated without decomposition in a silver vessel.

Action of Nitric Oxide upon Binoxide of Sodium.

The gas was prepared by the action of nitric acid upon copper, washed in a large volume of water, and dried by passage through sulphuric acid. The apparatus was filled with nitrogen before the introduction, and again before the withdrawal, of the boat containing the binoxide, to prevent the formation of hyponitric acid. The first signs of action appeared at a temperature of about 150° C. Portions of the substance became of a deeper colour and began to fuse. The whole was by degrees converted into a clear colourless liquid, an absorption of the gas taking place throughout. ·6456 grm. of binoxide of sodium were taken: the product weighed 1·1396 grm. These numbers are in the ratio of 100 : 176·5. According to the equation

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* Nitrous acid is immediately oxidized by an acid solution of binoxide of sodium. Besides the source of error mentioned above, the determination of nitrous acid with permanganate of potassium is liable to the objection that the reaction towards the close of the experiment proceeds very slowly.

$$Na_2 O_2 + N_2 O_2 = 2NO_2 Na.$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite of sodium.

Action of Nitric Oxide upon Tetroxide of Potassium.

From the analogy of the preceding reaction, it seemed probable that in this case a combination equally simple would lead to the formation of nitrate of potassium:

$$K_2O_4 + N_2O_2 = 2NO_3 K.$$

This, however, is certainly not the principal reaction, and probably does not take place at all. In three experiments, the product consisted of a mixture of nitrate and nitrite of potassium. In the first, the two were formed in atomic proportions: the relation was probably accidental, since, in the succeeding experiments, the proportion of nitrite was larger. The action was set up either in the cold or upon the application of a gentle heat. The yellow colour of the peroxide changed to white in parts gradually, in parts after first assuming a deeper tint and undergoing semi-fusion. Copious red fumes were formed, which passed on into the bulb-tube (nitric oxide being all the while slowly transmitted,) and formed crystals with the sulphuric acid which it contained. At the same time, an absorption of gas was apparent. When no further change could be observed, the nitric oxide was expelled from the apparatus, as before, by a current of nitrogen, and the boat and its contents removed and weighed. A second exposure to the action of the gas at a higher temperature produced no change in the weight.

1.—·3735 grm. of tetroxide of potassium yielded a product weighing ·488 grm.

2.—·2633 grm. of tetroxide yielded a product weighing ·3394 grm.

3.—·3752 grm. of tetroxide yielded a product weighing ·4737 grm.

These numbers, referred to 100 parts of the tetroxide, become,

1.	2.	3.
130·6	128·9	126·2.

If the product consist of nitrite, 100 parts of tetroxide of potassium should yield 119·7 parts; if of nitrate, 142·3 parts.

The product of Exp. 1 was dissolved in water, and the solution was divided into three equal parts.

a. Part 1 was determined with a standard solution of permanganate, to ascertain the amount of nitrite in the product. It required 24·77 c. c. 1 c. c. of the solution corresponded to ·000561 grm. of oxygen.

b. Part 2 was mixed with sulphuric acid, evaporated, ignited, and weighed. The weight of the sulphate of potassium thus obtained was ·1533 grm.

c. Part 3 was introduced into a flask containing solution of caustic potash and fragments of zinc and iron. The ammonia evolved on boiling was collected and determined by means of a standard acid solution.* It required 11·5 c.c. of a solution, of which 1 c. c. corresponded to ·00204 grm. of nitrogen.

From *a*, the total product must contain ·2215 grm. of nitrite of potassium, and therefore, supposing it to consist entirely of a mixture of the two, ·2665 grm. of nitrate. The supposition may be tested by comparing the proportion of potassium and nitrogen which such a mixture should contain, with the results of the determinations *b* and *c*. ·2215 grm. of nitrite of potassium contain by calculation ·1016 grm. of potassium and ·0365 grm. of nitrogen; ·2665 grm. of nitrate of potassium contain ·1029 grm. of potassium and ·0369 grm. of nitrogen.

		b.	*c*.
Total potassium in mixture	·2045	·2062	—
Total nitrogen	·0734	—	·0707.

The products of Exps. 2 and 3 were similarly determined with the same result.

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* The details of this method, which is both expeditious and exact, I hope to make the subject of a future communication.

Therefore, by the reaction of nitric oxide upon tetroxide of potassium, are formed hyponitric acid, and nitrate and nitrite of potassium in variable proportions. The only two palpable sources of variation are differences of temperature, depending upon the greater or less violence of the action, and differences in the time during which the hyponitric acid formed is in contact with the solid product, depending mainly upon the rate of transmission of the nitric oxide. The latter, I believe, to be the true cause of the variation in the product. If so, it is probable that three separate reactions play a part in producing the final result.

$$\begin{aligned}&(1.)\ K_2O_4 + N_2O_2 = K_2O_2 + N_2O_4;\\&(2.)\ K_2O_2 + N_2O_2 = 2KNO_2;\\&(3.)\ K_2O_2 + N_2O_4 = 2KNO_3.\end{aligned}$$

Long digestion, with a small quantity of nitric oxide, ought in this case to produce little but nitrate, and the action of a rapid current of the gas little but nitrite. Future experiments, especially upon the action of hyponitric acid on these peroxides, may decide this point.

XXII.—*Some Results of the Analysis of Commercial Coppers.*

By F. A. Abel, F.R.S.,

AND

Frederick Field, F.R.S.E.

The influence undoubtedly exerted by such metals as antimony, arsenic, and bismuth, in modifying the physical properties of copper, renders their detection, with certainty, when present in minute quantities, and their correct estimation, of considerable importance. Although many processes have been suggested for the determination of these metals, and especially of the two first named, chemists of considerable experience and ability are frequently found to differ widely in the results of their analyses of commercial copper from the same source, one chemist insisting, perhaps, on the presence of arsenic in very appreciable quantities, while another denies its existence in the same sample.

The causes of these discrepancies are well illustrated by the circumstance that one of the methods for the separation of arsenic from copper, most generally recommended in all works upon analytical chemistry, even in the very latest editions,—namely, the digestion of their sulphides in the sulphides of ammonium, sodium, or potassium, has been shown, by the experiments of Mr. Bloxam, to be altogether fallacious, when the arsenic does not exist in greater proportion than one per cent.; and that even one part of that metal, in conjunction with ninety of copper, cannot be detected by that method.

When it is remembered that, in the superior classes of refined copper, arsenic is seldom found in larger quantities than 0·10 per cent., and frequently only in proportions of from 0·02 to 0·05 per cent., it is very evident that, by pursuing the course above alluded to, no arsenic would be dissolved by the alkaline sulphides, and, consequently, the absence of that metal would be presumed.

The separation of *antimony* from copper, by means of sulphide of ammonium, does not appear, from Mr. Bloxam's experiments, to be attended by the same difficulties as in the case of arsenic. Mr. Bloxam's researches upon this portion of the subject merely show that when 1 per cent. of antimony is present in copper the metal may be detected in the sulphide of ammonium-solution; but, with regard to smaller quantities than this, we have no niformation.* From many experiments which we have instituted, it would seem that the detection of less than three-hundredths of a grain in one hundred grains of copper cannot be relied upon with any degree of certainty.

It also appears, from the experiments of the same chemist, that 20 or 30 per cent. of *tin*, when alloyed with copper, may be overlooked when the separation is based upon the solubility of sulphide of tin in sulphide of ammonium.†

In the case of arsenic, when in combination with copper, far smaller quantities may, however, be detected than those stated by Mr. Bloxam, if hydrosulphuric acid is passed through the solution, to which ammonia has previously been added, in excess. By adopting this method of operating, the arsenic is never precipitated, and consequently the separation is nearly, if not quite, complete. It is only necessary to saturate thoroughly with hydrosulphuric acid, in order to prevent traces of copper from entering into the ammoniacal liquid. For example:—

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* Quarterly Journal of the Chemical Society, Vol. v. p. 104.

† In a note (p. 370) appended to the last edition of Fresenius's Quantitative Analysis, the author says that M. Lucius, one of the students in his laboratory, has succeeded in effecting the complete separation of copper from tin, by means of yellowish sulphide of sodium, but it is indispensable to digest them three or four times with sufficiently large quantities of the solvent.

In a mixture of 10·00 grains of copper
and 0·10 grain of arsenic,

the latter was immediately detected, on the addition of hydrochloric acid to the filtered liquid.

In 10·00 grains of copper
mixed with 0·01 grain of arsenic,

the latter was discernible when the filtrate, mixed with excess of acid, had been kept in a warm place for half an hour.

Arsenic may, moreover, be detected in copper, in quantities not less than 0·20 to 100·00 of the latter, when the mixed sulphides are digested in strong sulphide of ammonium for many hours.

Although the rules laid down in analytical works, for the detection and separation of nearly every metal with which we are acquainted, appear, generally speaking, to be sufficiently plain and conclusive, every chemist must have experienced the difficulty of separating, or even distinguishing, very small quantities of metals, when associated with another in very much larger proportion. To take for example, the examination for tin, antimony, arsenic, and bismuth, of a specimen of refined copper which is supposed to be nearly pure, having passed through the various stages of its metallurgy, until the completion of the final operation. The copper would be dissolved in nitric acid, and water added; when, in the majority of cases, a turbidity in the liquid would be thereby produced. This might consist of antimonious or antimonic acid; arsenic, as arseniate of antimony; bismuth, thrown down from its solution as basic nitrate; lead, as sulphate (for if a trace of sulphur is present, sulphuric acid will be formed, and sulphate of lead consequently produced); and the whole of these compounds may weigh collectively only two- or three-tenths of a grain. Should either the nitric acid or water employed contain a trace of chlorine, silver, which is almost invariably found in copper, would also be separated, and add to the complexity of the precipitate.

Having ourselves individually experienced numerous difficulties such as those glanced at above, in the constantly recurring examination of specimens of commercial copper, we have devoted considerable attention to the improvement of the existing methods for the detection and correct estimation of its metallic impurities, and especially of antimony, arsenic, and bismuth; and in our researches on this subject we have, with the valuable co-operation of Mr. E. O. Brown, arrived at results which we believe are sufficiently important to analytical chemists, to warrant their publication.

The following is a method which, after various modifications, we have now employed for some time, with considerable success, both for the quantitative and qualitative examination of copper, when antimony, arsenic, bismuth, and lead, have to be detected and estimated.

About 200 grains of the metal are dissolved in nitric acid, a small quantity of solution of nitrate of lead is added, equal to about 10 grains of the salt, and subsequently an excess of ammonia and carbonate of ammonia. A precipitate is formed, which may consist of oxide and carbonate of lead, arseniate and antimoniate of lead, and oxide of bismuth, the whole of the copper remaining in solution. The precipitate is separated by filtration, thoroughly washed and digested in a strong solution of oxalic acid, whereby the antimony and arsenic are dissolved.

To the filtered liquid, sulphide of ammonium is added, or, what is preferable, it is rendered alkaline by ammonia, and hydrosulphuric acid is passed through to saturation. Traces of sulphide of copper generally impart a brownish tinge to the liquid, and are deposited after some time, as it is nearly impossible to wash away the last traces of that metal from the nitrate of lead-precipitate. This sulphide is filtered off, and a slight excess of hydrochloric acid is then added to the filtrate, which is diluted to about 8 ounces. If any large amount of either antimony or arsenic be present, there will be an immediate precipitate. If smaller quantities exist (one- or two-hundredths of a grain) the flask should be placed on the sand-bath for a few hours, and the temperature maintained at from 140° to 200° Fahr., when the metals, if present, will make their appearance as sulphides. If the precipitate be orange or orange-red, the presence of antimony is certain, but if of a pure canary-yellow, its absence may be presumed.

The precipitated sulphides are oxidized by means of concentrated nitro-hydrochloric acid, the clear solution is mixed with chloride of ammonium and excess of ammonia, and the arsenic is separated as the ammonio-magnesian arseniate ($2MgO, NH_4O, AsO_5, HO$). The filtrate from this is slightly acidified with dilute hydrochloric acid, and the antimony is precipitated by hydrosulphuric acid, and ultimately determined as antimoniate of teroxide of antimony (SbO_4). Should the presence of antimony and arsenic have been previously ascertained, it is, of course, unnecessary, in the quantitative process, to precipitate them both as sulphides from their solution in oxalic acid, as the arsenic may be at once precipitated by the addition of sulphate of magnesia and excess of ammonia, and the antimony determined in the filtrate.

In the determination of the *bismuth* and *lead* contained in copper, uniformly successful results have been obtained by employing the following method, which, as far as regards the separation of these metals from the copper and from any tin, antimony, or arsenic that it may contain, is founded upon the plan for detecting the arsenic and antimony just now described.

The nitric acid-solution of about 200 grains of the copper, is mixed with a small quantity of solution of phosphate of soda; ammonia in excess is then added; and the resulting precipitate is collected and purified from copper by washing with ammoniacal water. This precipitate is afterwards dissolved in hydrochloric acid, its solution is rendered alkaline with ammonia, and submitted to a current of hydrosulphuric acid. The precipitated sulphides of lead and bismuth are thoroughly washed, and dissolved in dilute nitric acid; the solution is nearly neutralized with ammonia, and then digested with a little hydrated oxide, or basic nitrate, of copper, which precipitates the oxide of bismuth, while lead remains in solution. The precipitate is thoroughly washed, dissolved in dilute nitric acid, and the bismuth separated from the copper by the addition of excess of ammonia; the oxide of bismuth thus obtained is purified by washing, and its weight determined in the usual manner. The solution containing the nitrates of lead and copper is mixed with solution of carbonate of soda; excess of acetic acid, and a small quantity of bichromate of potassa are added, and the chromate of lead is collected.

It should be observed that, in the event of the copper containing iron, that metal would be obtained as oxide together with the bismuth. When this is the case, which may readily be known by the brownish tinge imparted to the oxide of bismuth, they have to be separated. The mode of operation does not need description here.

The analytical methods just described are available not only for the determination of appreciable quantities of the metals antimony, arsenic, bismuth, and lead, but also for the detection of very minute proportions of those metals, and especially of the first two, when existing in copper.

In order to test the delicacy of the method described for the detection of minute traces of either arsenic or antimony, the following experiments were instituted:—

100 grains of electrotype-copper were dissolved in nitric acid, nitrate of lead was added, and afterwards a mixture of ammonia and carbonate of ammonia; the precipitate was boiled with solution of oxalic acid for half an hour, the dissolved portion filtered, and sulphide of ammonium added in excess. The few black flakes of sulphide of copper were separated by filtration, and hydrochloric acid was added to the filtrate. An opalescence was produced, which did not increase upon the application of gentle and long-continued heat, and did not assume any tinge of yellow: arsenic and antimony were therefore presumed to be absent.

Another 100 grains of the same copper were dissolved in a similar manner, and 0·1 grain of arsenic acid was added to the solution. The precipitate with nitrate of lead and carbonate of ammonia, treated as described above, gave an instantaneous indication of arsenic, which increased very much upon applying heat, the sulphide falling down in clear yellow flocks. Another similar quantity of the copper was tested with the addition of 0·05 grain of arsenic acid. The result was not so instantaneous, but, eventually, equally conclusive. 0·02 grain was then tried, with a similar confirmation; and even 0·01 grain of metallic arsenic, when dissolved in nitric acid, and added to the solution of the 100 grains of metallic copper, became, after some time, abundantly evident.

From these experiments, it appears that there is no difficulty whatever in detecting minute traces of arsenic in the presence of copper, the latter existing, in proportion to the former, as ten thousand to one.

A similar series of experiments was made upon the detection of antimony by this method. 0·10, 0·05, 0·02, and 0·01 grain were each added to four solutions of 100 grains of copper in nitric acid, and the results were quite as satisfactory as in the case of arsenic.

The presence of arsenic, even in a very small quantity of commercial hydrochloric acid, can be easily detected by this method. If a few drops of the acid be added to an ounce of water, nitrate of lead and excess of ammonia introduced, and the precipitate digested in sulphide of ammonium, the filtrate, on addition of hydrochloric acid and application of heat, shows abundant indications of arsenic.

Minute traces of this metal may also be satisfactorily recognized by the magnesia-test, as is shown by the following experiments: 100 grains of electrotype-copper and 0·10 grain of arsenic acid were dissolved in nitric acid. Ammonia was added in excess, and subsequently a small quantity of solution of sulphate of magnesia. In a few hours, a distinct crystalline precipitate was observed upon the sides of the glass, which proved to be the arseniate of magnesia and ammonia. 0·02 grain of arsenic was added to 100·00 grains of copper, and treated in the same way. The liquid was allowed to remain for a few days, and the slight sediment, containing a basic salt of copper, was digested in sulphide of ammonium. Hydrochloric acid, added to the filtrate, caused a precipitate, which, on heating, assumed a pure yellow tint.

A method, published by one of us, in the Chemical Gazette for 1857 (vol. xv., p. 113), seems also to be advantageous in the quantitative estimation of arsenic and copper. Oxalic acid, added to a slightly acid solution of the two metals, precipitates nearly the whole of the copper, leaving the arsenic dissolved. The great practical difficulty, is the tendency which oxalate of copper possesses, of passing through filtering paper, even when double or treble filters are employed. This difficulty, however, may be overcome by adopting the following mode of operation. Ammonia is added to the solution of the metals in sufficient quantity to throw down the oxide of copper, without redissolving it. Oxalate of ammonia, poured in excess upon this precipitate, effects its solution, forming a double oxalate of copper and ammonia. The introduction of nitric acid causes a precipitate of oxalate of copper, which can be filtered with great readiness. Sulphide of ammonium, added in excess to the filtrate, throws down the small quantity of copper which has escaped precipitation by oxalic acid, at the same time holding the arsenic in solution, which may be estimated in the usual manner. The following experiments were instituted at the time of publication:—

A mixture of 50 grains copper and 0·5 arsenious acid = 0·378 arsenic, gave 0·365 grains of arsenic.

With a mixture of 40 grs. copper and 0·10 grain of arsenic, decided indications of the latter were obtained.

It appears, from the above results on the comparative merits of the three methods detailed for the detection of arsenic in copper, that the plan of precipitation by means of nitrate of lead exhibits very decided superiority over the other methods, not only in point of delicacy, but also as regards facility and rapidity of execution. Thus, less than 0·01 grain of arsenic in 100 grains of copper is readily discovered by means of the nitrate of lead-process within two hours, while, for the detection of more than double that proportion of arsenic by the method of Levol (*i. e.*, by its precipitate as the ammonio-magnesian salt), at least forty-eight hours must elapse before any conclusion can be arrived at.

When compared with the very delicate process of testing copper for traces of arsenic recommended by Dr. Odling, the nitrate of lead-method also offers considerable advantages, being quite equal to it in point of delicacy, and susceptible of far more rapid application. Dr. Odling suggests, that the finely divided copper to be tested should be exposed for a few days to the joint action of pure cold hydrochloric acid and of air. The resulting liquid, and any copper that remains undissolved are to be transferred to a retort and carefully distilled, the mouth of the retort dipping into water. Special tests for arsenic are then to be applied to the product of distillation. The addition of a small quantity of chlorate of potassa to the hydrochloric acid is recommended, to accelerate the solution of the copper, care being taken to keep the metal in excess, so as to ensure the complete decomposition of the chlorate before distillation. Dr. Taylor directs, that any copper remaining undissolved, after two or three days' exposure to hydrochloric acid and air, should be removed before distillation, its weight being deducted from that of the copper originally employed.

If, instead of allowing the copper to remain in prolonged contact with hydrochloric acid and air, at ordinary temperatures, it is introduced, together with a little hydrochloric acid, into a capacious vessel, and exposed to a gentle heat, the results of the experiment are considerably modified. A specimen of copper, containing only a very minute trace of arsenic, and in which that impurity had been distinctly detected, both by the distillation-process, as just described, and by the nitrate of lead-method, was submitted to treatment with a small quantity of warm hydrochloric acid, in a Woulfe's bottle immersed in a water-bath. To this bottle were attached two others, the first containing water, into which the exit-tube of the heated bottle dipped, the second being partly filled with solution of acetate of lead. To the last bottle was attached a delivery-tube, which passed into a vessel containing a neutral solution of nitrate of silver. After continuing the application of heat for several hours, and examining the contents of the bottle containing water, in which any products of distillation had condensed, not a trace of arsenic could be detected, but in the nitrate of silver-solution was observed a very small black precipitate, resulting from the escape of hydride of arsenic from the apparatus. A similar experiment was made with a specimen of copper which contained about 0·3 per cent of arsenic. After exposure of this to heat, in contact with the acid, for a short time, it became coated with the grey film produced in applying Reinsch's test.[*] At the conclusion of the operation, which was continued for about four hours, no trace of arsenic was discovered in the condensed product, but an abundant precipitate was produced in the solution of silver. A specimen of copper, containing 1·1 per cent. of arsenic, was submitted to the same treatment for two successive periods of about two hours each. After both operations, the water in the condensing vessel contained only a very minute trace of arsenic, while the hydride of arsenic evolved was very considerable.[†]

It appears from these results that if, in exposing copper which contains arsenic to the action of hydrochloric acid, heat be applied, the arsenic will continue for a considerable period to pass off only in the form of hydride of arsenic, even if it be present in the copper in very considerable proportion; and that it might, therefore, readily escape detection in the distillation process, if heat were at once applied, to aid in the solution of the copper, for the purpose of shortening the time required for the application of the test, as directed by Drs. Tay or and Odling. If the process of heating be continued for a long period, the disengagement of hydride of arsenic gradually diminishes, and eventually ceases almost entirely, as the amount of copper in solution becomes considerable, and as the fragments of metal become perfectly coated with the grey arsenide.

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[*] This grey deposit, which consists, according to Lippert (J. f. prakt. Chem. v. 81, p. 168), of an arsenide of copper having the composition Cu_5As, makes its appearance only slowly when a slightly arsenical copper is exposed to the joint action of hydrochloric acid and air. But if the acid be mixed with about half its volume of the ordinary test-solution of pure sesquichloride of iron, a grey film is very speedily produced, if the copper contain only a trace of arsenic, in consequence of the comparative rapidity with which the solution of the copper is then effected. For the same reason, the contact, for an instant, of a fragment of chlorate of potassa, with the copper immersed in hydrochloric acid, will produce a grey stain upon the metal, even if the proportion of arsenic present be very small indeed. It need scarcely be stated that, under ordinary circumstances, these tests are only useful as affording a preliminary indication of the extent to which a specimen of copper is contaminated with such metals as arsenic, antimony, lead, or bismuth.

[†] Sublimates of arsenious acid were obtained by heating a portion of the delivery-tube through which the gas passed from the lead- to the silver-solution. The experiments were expedited by passing a slow current of air through the apparatus.

As a qualitative method of testing copper for arsenic and antimony, the plan of heating the metal with hydrochloric acid and carrying the evolved gas, purified as described, through nitrate of silver-solution, with the assistance of a slow current of air, can be recommended as comparatively very expeditious and exceedingly delicate; but, to identify each metal, when present in minute quantities, and to arrive at a knowledge of the proportion existing in the copper, by treatmen with hydrochloric acid, it is unquestionably necessary to effect the solution of the copper at ordinary temperatures, before distilling, and hence this method of examination is very tedious when compared with the process of separation by means of nitrate of lead and oxalic acid.

As regards the qualitative examination for *bismuth* in copper, considerable advantages, in point of delicacy and rapidity of execution over the quantitative method described in a former part of the paper, are possessed by a mode of testing for that metal, which is based upon a curious reaction exhibited by iodide of potassium in the joint presence of bismuth and lead, and which, we believe, has not hitherto been noticed. When iodide of potassium is added to a solution of a lead-salt, it is well known that yellow iodide of lead is precipitated, which dissolves on heating the liquid, and is re-precipitated, on cooling, in brilliant golden-coloured scales. (The solution of the amorphous iodide may be greatly facilitated by the addition of a small quantity of hydrochloric acid.) If the least trace of bismuth is present in the lead-salt, the re-precipitated scales are no longer yellow, but assume a dark orange or crimson tint, varying in intensity of colour according to the amount of bismuth present. This test is of such extraordinary delicacy, that 0·00025 of a grain of bismuth may be detected in copper with the greatest ease, the iodide of lead becoming dark orange, while 0·001 grain imparts a reddish-brown tinge, and 0·01 grain a bright crimson, the scales resembling chromate of silver in appearance.

The mode of operation in applying this test is as follows:—About 100 grains of the copper to be examined are dissolved in nitric acid, a solution of nitrate of lead, equal to about 5 grains of the salt, is added, and subsequently ammonia and carbonate of ammonia. The precipitate is washed with ammoniacal water, to free it from copper, and dissolved in warm acetic acid. Considerable excess of iodide of potassium is introduced, and the liquid is warmed until the precipitate disappears. On cooling, the crystalline scales will shew, by their colour, the presence or absence of bismuth.* If in the same specimen of copper it is desired to test for arsenic and antimony, the nitrate of lead-precipitate is digested with oxalic acid. The oxalates of lead and bismuth are insoluble in acetic acid, and must therefore be dissolved in as small a quantity as possible of hydrochloric acid.

By the employment of the test just described, bismuth has been detected in many specimens of very pure copper. Nearly all the modern copper-coinage, more especially that of the reigns of George III. and IV., contains very considerable traces, and in the new bronze-currency it is abundantly evident. It is found also in the silver money of England, as well as of other countries, owing, probably, to the copper with which it is alloyed. Copper which has been rolled out to a ribbon, has been found to contain it to the extent of at least 0·02 per cent., while in some specimens of commercial sheet copper, as much as between 0·10 and 0·20 per cent. has been discovered. It may also be traced in nearly all copper gauzes, wires, and foil.

It might be presumed, from the nature of the methods described at the commencement of this paper, that bismuth would be separated from antimony and arsenic by means of oxalic acid. Numerous experiments have proved this to be the case. The precipitate occasioned by nitrate of lead, after digestion in oxalic acid, is entirely deprived of any antimony or arsenic with which it might have been previously associated, while the whole of the bismuth remains undissolved.

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* Iodide of lead is very soluble in the acetates of soda, potassa, and ammonia, even in the cold, forming colourless solutions, from which iodide of potassium, added in excess, precipitates iodide of lead in the crystalline state, although no heat has been applied. Gmelin, in mentioning many solvents of this compound, does not allude to the acetates of the alkalies, which dissolve it with infinitely greater ease than any of the others which are mentioned.

We append to this paper a tabular statement of the results obtained by an application of the methods of analysis, specially recommended in this paper, to the qualitative and quantitative examination of a large number of varieties of copper, which includes specimens of blister, bar, and refined copper from Chile, Mexico, Australia, North America, Buenos Ayres, Manilla, Spain, Russia, Sweden, Norway, Italy, and Hungary; numerous specimens of English "*best-select*" copper, of sheet and bolt-copper, and also several English and foreign coins.

The results of these examinations lead us to the following conclusions regarding the principal metals associated with copper:

1°. Arsenic and silver are almost invariable impurities in copper;

2°. The occurrence of bismuth in copper is very general; this metal seems to be absent only in those cases in which carbonates of copper have been alone employed in the production of the metal, as in the majority of Australian and Russian coppers;

3°. Antimony is not nearly so general an impurity of copper as has been supposed. There appears little doubt that, in analyses for practical purposes, the bismuth existing in copper has been mistaken for antimony, inasmuch as the rough qualitative method of testing, by the addition of a large quantity of water to the strong solution of copper in nitric acid, commonly employed, furnishes a white precipitate which has been regarded as an indication of antimony;

4°. Lead is of very rare occurrence in cake-copper, both unrefined and refined, as sent into the market; but appears to be an almost invariable constituent of copper which has been manufactured into sheet or rod.

It may be observed, in conclusion, that iron, which, like sulphur, exists, as might be supposed, in considerable proportions in what is technically termed bar copper, is almost perfectly removed by the refining process.

RESULTS of the Examination for Metallic Impurities, of different varieties of Copper.

Description of Copper.	Silver.	Arsenic.	Anti-mony.	Bismuth.	Lead.	Tin.	Iron.
BAR AND BLISTER COPPER.							
Chile, No. 1 Bar	Silver was detected in all these specimens, but not determined.	traces	..	traces	..	..	0·62
,, 2 ,, ...		traces	..	..	..	..	0·71
,, 3 ,, ...		traces	..	traces	..	..	0.85
,, 4 ,, ...		0·10	..	traces	..	..	0·91
,, 5 ,, ...		traces	traces	traces	..	..	0·62
,, 6 ,, ...		traces	..	traces	..	..	0·46
,, 7 ,, ...		traces	..	traces	..	..	0·52
,, 8 ,, ...		traces	..	traces	..	..	0·67
,, 9 ,, ...		traces	..	traces	..	..	0·64
,, 10 ,, ...		traces	traces	traces	..	..	0·52
,, 11 ,, ...		traces	..	..	..	..	0·62
,, 12 ,, ...		0·02	traces	..	..	..	0·50
,, 13 ,, ...		0·04	traces	..	..	..	0·43
,, 14 ,, ...		0·07	0·50	traces	..	..	0·51
,, 15 ,, ...		..	..	..	..	..	0·84
,, 16 ,, ...		0·40	traces	traces	..	..	1·64
,, 17 ,, ...		0·45	..	..	..	..	1·52
,, 18 ,, ...		traces	..	..	..	..	0·70
,, 19 ,, ...		0·50	0·20	..	..	..	0·08
,, 20 ,, ...		..	..	..	..	..	1·20
,, 21 ,, ...		..	traces	traces	..	..	0·98
,, 22 ,, ...		..	traces	traces	..	..	1·00
,, 23 ,, ...		traces	..	traces	..	..	1·20
,, 24 ,, ...		traces	..	traces	..	..	1·04
,, 25 ,, ...		traces	..	traces	..	..	1·12
,, 26 ,, ...		traces	..	traces	..	..	1·02
,, 27 ,, ...		traces	..	traces	..	..	0·84
,, 28 ,, ...		0·03	traces	traces	..	..	1·10
,, 29 ,, ...		..	..	..	..	..	0·75
,, Blister Copper ..		0·10	traces	traces	..	..	0·32
Matzatlan Copper		traces	..	traces	..	..	1·32
New Mexican		..	..	..	..	..	0·42
Spanish, No. 1		3·31	0·70	..	..	..	traces
,, 2	..	2·49	..	trace	..	..	,,
,, 3	..	2·15	..	0·04	trace	..	,,
,, 4	..	1·18	..	..	trace	..	,,
,, 5	Silver was detected in all these specimens, but the quantities were not determined.	1·20	..	trace	..	..	,,
,, 6		0·90	..	..	..	..	,,
,, 7		0·30	..	..	..	..	0·21
,, 8		0·25	..	traces	..	..	0·35
Swedish, No. 1		0·25	0·20	..	..	..	0·31
,, 2		..	traces	..	..	..	0·20
Manilla Slab		1·24	0·65	0·05	..	..	traces
Buenos Ayres Slab		0·31	0·17	0·10	..	..	traces
Australian (Sydney)		..	..	..	..	..	1·01
,, (Sydney)		..	..	..	..	..	0·76
REFINED COPPERS.							
Chile, (Societé Italienne) ..		..	..	..	..	..	0·01
Chile, No. 2		0·04	..	..	..	..	0·03
,, 3		0·03	..	..	..	..	..
Spanish		traces	..	..	..	..	0·06
,, No. 2		0·63	..	..	..	..	..
Italian, No. 1		..	..	trace	..	..	..
,, 2		..	..	..	..	..	trace
Tuscan Rosette		..	..	trace	..	..	trace

Results of the Examination for Metallic Impurities, of different varieties of Copper.

Description of Copper.	Silver.	Arsenic.	Antimony.	Bismuth.	Lead.	Tin.	Iron.
Russian (C.C.N.D.)	Present but not determined.	0·11	..	minute traces	..	..	..
„ No. 2		..	..	..	..	..	0·30
Hungarian		0·36	0·22	traces	..	..	trace
„ Rosette		0·06	0·12	..	..	..	„
Australian (Burra Burra) ..	..	0·02	..	..	..	..	trace
„ (Kapunda) ..	..	0·01	..	..	..	..	trace
Lake Superior	0·07	0·01	..	..	..	..	trace
Norwegian (Alten)	trace	..	..	..	..	..	trace
North American	0·22	..	..	..	..	..	trace
„ No. 2 ..	0·06	..	..	..	..	..	trace
„ No. 3 ..	trace	..	..	..	..	..	trace
English Tile	traces	0·07	traces	0·02	..	..	trace
English Best Select, No. 1	0·03	0·03	..	0·05	..	..	trace
„ „ No. 2	0·02	0·04	..	0·04	..	..	trace
„ „ No. 3	0·02	0·01	..	0·05	..	..	trace
„ „ No. 4	0·03	0·04	..	0·04	..	..	trace
„ „ No. 5	0·02	0·12	0·02	0·05	..	..	trace
„ „ No. 6	0·04	0·15	0·05	0·05	..	..	trace
„ „ No. 7	0·03	0·14	0·02	0·04	..	..	trace
„ „ No. 8	trace	0·13	0·07	trace	..	..	trace
„ „ No. 9	trace	trace	trace	trace	..	..	trace
„ „ No. 10	0·03	0·14	0·05	0·05	..	..	trace
„ „ No. 11	0·07	0·31	trace	0·17	..	..	trace
„ „ No. 12	0·05	0·15	trace	0·12	..	..	trace
„ „ No. 13	0·05	0·12	trace	0·13	..	..	trace
„ „ No. 14	0·05	0·14	trace	0·12	..	..	trace
„ „ No. 15	0·06	0·10	..	0·12	..	..	trace
„ „ No. 16	0·02	0·04	0·02	trace	..	..	trace
„ „ No. 17	0·03	0·06	..	0·04	..	..	trace
SHEET AND BOLT COPPER.							
Sheet, No. 1	0·07	trace	trace	0·13	0·07	..	trace
„ No. 2	0·05	0·08	0·02	0·09	0·15	..	trace
„ No. 3	0·07	0·12	trace	0·06	0·08	..	trace
„ No. 4	0·02	0·14	..	0·04	0·05	..	trace
„ No. 5	0·05	0·09	..	0·13	0·25	..	trace
„ No. 6	0·06	0·10	0·01	0·18	0·18	..	trace
„ No. 7	0·03	0·10	trace	0·10	0·40	..	trace
„ No. 8	0·05	0·06	trace	trace	0·15	..	trace
„ No. 9	0·03	0·12	trace	0·05	0·38	..	..
Bolt, No. 1	trace	0·07	..	0·02	0·13	trace	trace
„ No. 2	trace	0·01	..	0·02	0·22	trace	trace
COINS.							
Copper Coin, George III. ..	All these specimens contained silver, the proportions were not determined.	0·12	trace	trace	..	..	trace
„ „ George IV. ..		0·09	trace	trace	..	trace	trace
„ „ William IV. ..		0·04	..	trace	..	trace	trace
New Bronze Coin		trace	..	trace	..	not estimated	trace
Spanish Coin, 1856		0·30	..	trace	..	trace	0·03
Chile Coin 1858		trace	..	trace	..	trace	0·04
United States Coin, 1849 ..		trace	..	trace	..	trace	trace
Chinese Coin		trace	..	0·04	..	trace	0·12
Old Italian Coin		trace	..	..	..	trace	0·21
*Bactrian Coin (181 B.C.) ..		..	..	trace	..	..	trace
Dutch Coin		..	..	trace	..	0·17	..
Copper rolled into thin ribbon		..	..	0·03	..	..	..

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* This coin was kindly given to us by Walter Hawkins, Esq., from his valuable collection.

XXIII.—*On the General Distribution of Bismuth in Copper Minerals.*

BY FREDERICK FIELD, F.R.S.E.

FROM the paper I had the honour of submitting to the Society, in conjunction with Mr. Abel, upon the metallic impurities in commercial coppers, it will have been observed, that many of the samples analysed were found to contain bismuth.

This metal was particularly sought for, owing to an opinion that bismuth, even in minute quantities, exercises a decidedly injurious effect upon copper. As it was detected in coppers brought from many parts of the world, it occurred to us that it must necessarily be associated very widely indeed with copper minerals, and probably existed as frequently with the sulphides of that metal, as sulphide of silver is known to exist with the sulphide of lead. It was necessary, in order to determine this fact, to make a very extended investigation of the minerals of copper from various sources, and, as far as possible, to be acquainted with the locality, and even the name of the mine, from which the specimens, intended for analysis, were derived, and I have been fortunate enough to obtain samples from some of the leading mineral districts with which we are acquainted. The investigation embraces analyses of different varieties of copper ore from England, Scotland, Ireland, Wales, France, Spain, Turkey, Russia, Africa, and Australia; as well as Chile, Peru, Mexico, the United States, Canada, and Cuba. It is to be regretted that specimens from Germany and other countries were not received in time to admit of publication in this paper. The method pursued for the qualitative estimation of bismuth, is described in the preceding paper; and it is merely necessary to mention, that it depends upon the extraordinary influence exerted by a salt of bismuth, when precipitated together with a lead-salt by iodide of potassium, a minute trace of the former metal imparting a strong red tinge to the yellow iodide, which is seen to greater advantage, when the double salt is dissolved in very dilute hydrochloric acid, at the boiling temperature, and allowed to cool slowly. As, in the majority of copper ores, iron exists to a very great extent, and is necessarily precipitated by ammonia, together with the lead and bismuth, it is more convenient to dissolve the mineral to be examined, in nitro-hydrochloric acid, expel all traces of nitric acid by boiling, and after filtration, precipitate the copper and bismuth upon metallic iron. After digestion in nitric acid, the examination may be conducted as previously directed. As the list of nearly fifty examinations, appended to this memoir, only includes those minerals in which bismuth has been found, it may be as well to cite a few instances in which it could not be detected.

Bismuth is absent in all the oxides, carbonates, and metallic coppers of Chile. In the phosphates (*Liebethenite* and *Tagilite*), and in the silicates *Chrysocolla* and *Dioptase;* in the arsenides *Domeykite* and *Algodonite,* and in the highly sulphuretted mineral *Guayacanite* ($3Cu_2S. As\ S_5$). It could not be recognized in the malachites from Siberia, Russia, Australia, and the west coast of Africa, nor in a specimen of double sulphide of copper and iron (Cu_2S,Fe_2S_3) from Coquimbo. Many other specimens (free from sulphur) were examined, but no bismuth could be obtained.

The conclusions deducible from the above experiments must lead us to suppose, that bismuth is seldom or never found in copper minerals free from sulphur; but on the other hand, that it is nearly always found in conjunction with the sulphides. The two instances just related, in which it is absent, are exceptions to the constancy of its presence, and it may be concluded that it exists to as great an extent, and in about the same proportion with sulphide of copper, as sulphide of silver to sulphide of lead.

It may be mentioned, that Mr. John Abel detected bismuth as tersulphide in some copper minerals in Copiapo; a fact which is rather interesting, as it was the first instance in which bismuth was found associated with copper in that part of South America.

COPPER MINERALS in which Bismuth has been detected.

No.	Locality.	Name of the Mine.	Copper per cent.	Bismuth.
1	Chile (Coquimbo)	Pique	44·12	Bismuth.
2	„ „	Chaleco	38·58	„
3	„ „	San José	42·64	„
4	„ „	Tortolas	12·20	„
5	„ „	Mollaccas	56·25	„
6	„ (Huasco)	Rosario	14·60	„
7	„ „	Bronce	16·81	„
8	„ (Coquimbo)	Rosario	11·20	„
9	„ „	Menillas	18·40	„
10	„ (Copiapo)	Checo	21·20	„
11	„ „	Cerro Negro	24·62	„
12	„ (Copiapo)	Tres Puntas	21·40	„
13	„ „	Unknown	19·70	„
14	Peru (Tacna)	„	21·20	„
15	„ (Tacna)	„	14·10	„
16	„ (Tacna)	„	36·28	„
17	Mexico (Zacatecas)	„	11·20	„
18	„ (Somelhuacan)	„	21·00	„
19	„ (unknown)	„	2·80	„
20	„	San Salvador	37·70	„
21	Cuba	Unknown	14·40	„
22	„	„	23·50	„
23	„	„	12·50	„*
24	„	Cobre	22·40	„*
25	Canada West	Lake Huron	22·50	„*
26	North Carolina	Unknown	19·40	„
27	Ireland	Beachaven	12·60	„*
28	Wales (Anglesea)	Parry's Mine	21·60	„*
29	England (Cornwall)	East Caradon	9·90	„
30	„ „	West Caradon	23·00	„
31	„ „	South Caradon	9·90	„
32	„ „	Great Wheal Martha	4·70	„
33	„ „	Phœnix Mines	15·30	„
34	„ „	Devon and Cornwall United.	3·70	„
35	„ „	Great Wheal Busy	5·40	„
36	„ „	Fowey Consols	6·90	„
37	„ „	United Mines	5·20	„
38	„ „	Treleigh Consols	5·80	„
39	„ „	Craddock Moor	9·80	„
40	„ „	Pembroke	7·10	„
41	„ „	North Wheal Busy	11·90	„
42	„ (Devonshire)	Devon Great Consols	5·00	„
43	France	Unknown	7·20	„
44	Spain	Garrucha	17·60	„
45	„	Del Soto	17·40	„
46	„	Unknown	9·40	„
47	Turkey	„	13·20	„
48	Africa	Ookip	36·90	„
49	Australia	Wheal Maria	27·70	„

* These specimens had very minute traces.

XXIV.—*On Leucic Acid and some of its Salts.*

By J. Louis W. Thudichum, M.D.

Preparation.—When pure leucine is dissolved in warm water and treated with nitrous acid gas, it is decomposed, with evolution of nitrogen. The liquid froths very much, and assumes a reddish colour. When the reaction ceases, which is generally the case after three or four hours, the fluid is evaporated to a small bulk or syrupy consistence on the water-bath, and allowed to cool. If, as should be the case, a quantity of undecomposed leucine is present, the fluid shoots into a crystallised mass of nitrate of leucine surrounded by a syrupy acid. This mixture is transferred to a stoppered bottle, and treated with repeated quantities of ether, which dissolves leucic acid, leaving nitrate of leucine in splendid crystals undissolved. Crystals and solution are separated by the filter, the ether is distilled off the filtrate, and the syrupy residue, of a slightly yellowish colour, is evaporated on the water-bath for a short time. It is next dried over sulphuric acid, when overnight crystallisation begins from the margin of the syrup, which, in the course of a few days, involves the whole liquid.

From the watery solution in which it was found, leucic acid may be extracted by ether directly, without the assistance of preliminary evaporation. In this case, the solution must be treated with repeated quantities of ether, otherwise much leucic acid remains in solution. When evaporation is had recourse to, it is best to add a little leucine to the fluid, which combines with the free nitric acid, and prevents it from exerting any oxydizing influence upon the leucic acid.

Properties.—The crystals are needles placed in radiary arrangement, the centres being at the periphery of the surface of the liquid where it touches the dish. The crystallised masses have the lustre of mother-of-pearl, with a beautiful variety of concentric markings, resembling the markings of some descriptions of larch agarics, in a much higher degree than the clusters of leucine itself, which have been so described.

Impure and dark-coloured leucic acid crystallises much more slowly than the pure acid. It requires about a week of standing over sulphuric acid, before a start is effected, and even then the formation of crystals proceeds but slowly.

Purification.—The acid thus obtained may be purified after crystallisation by re-solution in cold water and filtration. An insoluble dark-brown oily matter remains on the filter. The crystallised acid may also be pressed between folds of bibulous paper; but unless a good press or a vice be employed, much liquid will not be removed thereby. On the whole, the purification of leucic acid is a difficult and tedious process. The greatest care should therefore be taken to employ pure leucine for the production of the acid. Nevertheless, the apparently purest leucine not unfrequently yields a yellow solution. This is best treated with acetate of lead, which precipitates leucate of lead in white copious flakes, to be dissolved in boiling alcohol after washing with water; the precipitate, after washing with cold alcohol, and suspension in water, is to be decomposed by hydrosulphuric acid. The watery solution should be evaporated on the water-bath at a very low temperature or over sulphuric acid.

Chemical Properties.—Leucic acid cuts under the knife like hard soap, almost like stearic acid, and is very soluble in water. A small piece, placed in water, is rapidly dissolved, producing curious currents of diffusion. This phenomenon is most remarkable when watched with the aid of the microscope.

Leucic acid is heavier than water. Its solution has an agreeably acid taste, reddens litmus, and decomposes carbonates, the acid combining with their bases.

It is soluble in alcohol and ether.

When heated below the boiling point of water, it fuses, and, on cooling, solidifies again. When the heating in the water-oven is continued for several hours, the evolution of acid-smelling vapours is continually perceived. On cooling, the acid does not, however, again solidify; it becomes more consistent, but remains an uncrystallisable, dark-brown, smeary syrup, which, after standing for weeks over sulphuric acid, undergoes no change, and is found to be nearly insoluble in water, separating from it like oil, and sinking to the bottom. It emits a very disagreeable odour. When leucic acid, even in dilute solutions, is heated to the boiling point, or when its solution is evaporated, a small quantity of this insoluble compound is always formed. It is the admixture of this substance which makes the production of pure salts of leucic acid a matter of some difficulty. This peculiar change also explains the statement which I have seen put forth in Schlosser's "Handbuch der Chemie," that leucic acid is not crystallisable. It is highly crystallisable, but easily becomes transformed into an uncrystallisable body, by exposure to a temperature not exceeding the boiling point of water. The properties of the new substance I have not studied any further.

When heated strongly, leucic acid gives out thick fumes, and blackens, then takes fire and burns with a fuliginous dark-yellow flame, leaving a small quantity of charcoal, which is quickly and easily consumed.

Composition and Analyses.—I. 6·447 grains of crystallised acid, dried over sulphuric acid, and burnt from a platinum boat in a current of oxygen, yielded 12·703 grains of carbonic acid and 5·047 grains of water, corresponding to 53·73% of carbon and 8·68% of hydrogen.

II. 5·473 grains yielded 10·792 grains of carbonic acid and 4·337 grains of water, corresponding to 53·77% of carbon and 8·80% of hydrogen.

III. 5·645 grains yielded 11·220 grains CO_2 and 4·402 HO, equal to 54·20% C, and 8·66% H.

			Found.		
	Equivalents.	In 100 parts.	I.	II.	III.
C_{12}	72	54·54	53·73	53·77	54·20
H_{12}	12	9·09	8·68	8·80	8·66
O_6	48	36·37	,,	,,	,,
	132	100·00			

Taking into consideration the known formula of leucine, $C_{12}H_{13}NO_4$, and the equivalent of leucic acid, as ascertained by the analyses of some of its salts stated below, the above figures lead to the formula $C_{12}H_{12}O_6$.

Both carbon and hydrogen were found too low in the analyses, while the same acid furnished salts, which, like that of cobalt, yielded the most accurate figures on analysis. On re-solution of another portion of the acid, used for combustion, it was found that a small portion had again been transformed into the dark, oily body insoluble in water.

The mode of burning leucic acid in the platinum boat, in a current of oxygen, is not the most suitable, as in case the acid is heated a little too rapidly, explosions are likely to ensue within the combustion-tube, which easily disarrange the apparatus and cause the loss of the analysis.

Leucate of Ammonia.—Leucic acid neutralised with ammonia in slight excess, and evaporated, leaves a thick homogeneous residue, in which no crystallisation can be observed, even after it has been drying over sulphuric acid for several weeks.

Leucate of Soda.—A watery solution of leucic acid, carefully saturated with carbonate of soda and evaporated, leaves a syrupy residue covered with a crystalline crust. On standing over sulphuric acid, crystals form in the syrup, which, under the microscope, have a characteristic tub-shape, with rhombic plates interspersed here and there. The crystals could not be sufficiently isolated and purified for analysis.

Leucate of Lime.—$C_{12}H_{11}CaO_6$. A dilute solution of leucic acid, while boiling, is neutralized with carbonate of lime. The filtrate, on evaporation, yields crusts of a salt which I have not been able to observe in a crystalline state. The salt cannot be purified by recrystallisation, and retains the yellow colour which it assumed during boiling.

I. 0·776 grm., dried at 100° C., yielded 0·337 grm. of sulphate of lime, corresponding to 12·78% of calcium.

II. 0·588 grm. gave 0·2535 grm. of sulphate, corresponding to 12·68% Ca.

	I.	II.	Calculated.
Ca	12·78	12·68	13·24

Leucate of Magnesia.—A very dilute solution of leucic acid is neutralized with carbonate of magnesia. The salt is very little soluble in water, and, like the zinc-salt, is deposited in crusts on evaporation.

Leucate of Baryta.—A dilute watery solution of the acid is neutralized with the carbonate while boiling. After filtration and evaporation, crystalline crusts of the salt are obtained. Pressed between bibulous paper and dried, the salt retains a yellow colour.

Leucate of Cobalt.—A dilute aqueous solution of leucic acid is boiled with an excess of carbonate of cobalt. The rose-coloured filtrate, on evaporation, deposits light crusts of a pink colour while moist, but of a very pale rose colour, or almost white when dry. This salt is not much more soluble in boiling than in cold water. Its solubility in this menstruum is, on the whole, limited.

It crystallises in needles, which, when seen under the microscope, appear arranged in globular masses. To the naked eye these globules appear as little warts imbedded in crusts showing no structure.

Analyses and Composition.—I. 7·9 grains, on combustion, left 24·55%; viz., 1·94 grains of residue, being Co_3O_4, of which, theoretically, 25·25% should be left. After treatment with nitric acid and exposure to heat, the percentage value of the residue rose to 26·49%, but fell again to 23·54% after prolonged exposure to a light red heat. After reduction with hydrogen, there were left 1·46 grains of metallic cobalt, corresponding to 18·48%.

II. 2·570 grains, on combustion, left 0·62 grains, or 24·12% Co_3O_4; and, on treatment with hydrogen, left 0·470 grains Co, equal to 18·28%.

These figures again show that no constant compound of oxygen and cobalt can be obtained by exposure of a salt to heat, and that cobalt must be quantitatively determined in its metallic state.

The average of the two determinations exactly corresponds with the theoretical amount; viz., 18·38%.

III. 0·4615 grm., on combustion with oxyde of copper, yielded 0·7611 grm. of carbonic acid and 0·2802 of water, corresponding to 44·97 per cent. of carbon and 6·75% of hydrogen.

IV. 0·280 grm. yielded 0·4586 grm. CO_2 and 0·1712 grm. HO, corresponding to 44·67 C, and 6·79% H.

			Found.			
	Equiv.	In 100 parts.	I.	II.	III.	IV.
C_{12}	72	44·85	,,	,,	44·97	44·67
H_{11}	11	6·85	,,	,,	6·75	6·79
Co	30	18·38	18·48	18·28	,,	,,
O_6	48	,,				
	161					

Leucate of Zinc.—Dilute leucic acid, while boiling, is treated with carbonate of zinc. The salt in solution is filtered while boiling hot. If the solution of leucic acid was not exceedingly dilute, a thick froth, containing undissolved salt and carbonate, is formed at the top of the liquid, which requires repeated boiling with water before it is dissolved. The latest solutions are the purest and least coloured. The solution of the leucate deposits a thin crust on cooling. On evaporation over the water-bath, it soon becomes covered with a crust, and on cooling, deposits voluminous masses of needles. They are separated by the filter, pressed between bibulous paper, and dried by exposure to air, or over the water-bath.

The salt is white, like snow, and of a splendid silky lustre. Under the microscope, masses of needles are observed, which, in the crusts, are seen to form dark globular masses. It is little soluble, even in boiling water; less soluble in cold. At 100°C., the salt parts with little more than half the moisture which it retains when air-dry. It requires a temperature between 120° and 130°C. to dry it completely.

Hydrosulphuric acid precipitates only a portion of the zinc from a solution of the salt. Even after repeated saturation of dilute and concentrated solutions with this gas, such an amount of zinc remains in the liquid, that, on concentration and cooling of the solution, the zinc-salt crystallizes in splendid needles. The best mode of producing the zinc-salt in a pure and crystallised state, is to let it crystallise from an excess of leucic acid.

Analyses and Composition.—

			Found.				
	Equiv.	In 100 parts.	I.	II.	III.	IV.	V.
C_{12}	72·0	44·01	43·83	43·95	43·84	,,	,,
H_{11}	11·0	6·72	6·79	7·08	6·82	,,	,,
O_5	40·0	24·45	,,	,,	,,	,,	,,
ZnO	40·6	24·82	,,	,,	,,	25·45	24·65
	163·6	100·00					

I. 0·4243 grm. of salt, on combustion with oxide of copper, gave 0·6820 grm. of carbonic acid and 0·2596 grm. of water, corresponding to 43·83% C and 6·79% H.

II. 0·2850 grm. of substance yielded 0·4593 grm. CO_2 and 0·1817 grm. HO, corresponding to 43·95% C and 7·08% H.

III. 0·320 grm. of salt gave out 0·5143 grm. CO_2 and 0·1965 grm. HO, equal to 43·84% C and 6·82% H.

IV. 0·4380 grm. of salt, dissolved in hydrochloric acid, precipitated with carbonate of potassa, after exposure to red heat, left 0·1115 grm., corresponding to 25·45% ZnO.

V. 7·923 grains of salt, dissolved in hydrochloric acid, and precipitated by carbonate of soda while boiling, yielded 1·958 grain, or 24·65% of ZnO.

Leucate of Suboxide of Mercury.—When to a solution of leucic acid a solution of nitrate of suboxide of mercury is added, a slight turbidity ensues. The addition of carbonate of soda produces a copious reddish-white precipitate, which, on boiling, becomes red, then dull grey, and deposits metallic mercury at the bottom of the tube.

Leucate of Oxide of Mercury may be prepared,—

a. Directly, by dissolving freshly precipitated moist oxide of mercury in an aqueous solution of leucic acid. A flaky precipitate gradually ensues, which, on heating, becomes red and granular, and adheres to the sides of the glass. On cooling, a new precipitate, consisting of whitish globules, is deposited.

b. By adding nitrate of protoxide of mercury to an aqueous solution of leucic acid. A whitish-red precipitate is then formed, which dissolves on boiling, and, on cooling, is again deposited in reddish granules.

c. By adding the mercurial solution to the leucate of an alkali.

The leucates of both oxides of mercury have a great tendency to become reduced. The salt of the oxide easily passes into that of the suboxyde. The salt of the oxide, moreover, has a great tendency to become basic and insoluble. For these reasons, the salts have not been analysed.

Leucate of Copper.—When a dilute aqueous solution of leucic acid is treated with a dilute solution of ammonio-sulphate of copper, the colour of the copper-salt changes to light green. On boiling the liquid, it becomes paler, and, on cooling, deposits light green granules of leucate of copper. Under high powers of the microscope, these granules appear as balls, formed by a radiary arrangement of needles. The smallest balls are more suitable for seeing this arrangement than the larger ones, which are not sufficiently transparent.

The salt is very little soluble in cold,—more soluble in boiling water. Dried at 130°, it left, on combustion in the platinum crucible and treatment of the residue with nitric acid and renewed exposure to heat, a quantity of oxide which corresponded to 23·26%.

	Equivalents.	In 100 parts.	Found.
C_{12}	72	,,	,,
H_{11}	11	,,	,,
O_5	40	,,	,,
CuO	39·68	24·3	23·26
	162·68		

Leucate of Silver.—A hot dilute solution of leucic acid decomposes recently prepared carbonate of silver with effervescence. The excess of the silver and the undissolved portion of the leucate become blackish-grey, but the acid is not entirely neutralized. The hot filtrate forms no deposit on cooling. The attempt to evaporate it over the water-bath produces a black precipitate of reduced silver. It must, therefore, be evaporated under the air-pump with the aid of sulphuric acid. After prolonged standing, a few crystals, of a glassy lustre and appearing under the microscope as groups of rhombic plates, are deposited at the margin of the dish. The liquid then becomes covered with a pellicle, and evaporation is impeded. At a later stage, conglomerates of needles are deposited, which, when carefully dried over sulphuric acid in vacuo, appeared a little blackened, like most silver-salts, but not decomposed. 0·4606 grm. yielded 0·1242 grm. of silver, equal to 26·97 per cent. The bileucate of silver $(C_{12}H_{11}AgO_6)+\cdot C_{12}H_{12}O_6$, requires 29·1% of silver.

By adding nitrate of silver to a warm solution of leucate of potassa, or soda, or ammonia, a copious, white, amorphous precipitate is produced, which increases as the liquid cools. It soon blackens when allowed to stand in the mother-liquor. Filtered, washed, and dried over sulphuric acid, it yielded by analysis the following result:—

2·186 grains left, on combustion, 0·965 grain of silver, or 44·14%.

	Equivalents.	In 100 parts.	Found.
C_{12}	72	,,	,,
H_{11}	11	,,	,,
Ag	107·97	45·18	44·14
O_6	48	,,	,,
	238·97		

On drying over the water-bath below 100°, this salt became brown, and continued to lose weight. After many useless attempts, I abandoned its further analysis.

Leucate of Lead.—On adding acetate of lead to a solution of leucic acid, or a suitable leucate, a copious white precipitate is produced, which is flaky, and, on boiling, almost entirely dissolves in the fluid. Any portion remaining undissolved melts into a white mass, which is soft like resin while warm, but becomes brittle and hard on cooling. This substance is insoluble in water and alcohol, even on boiling, and seems to be a basic salt.

If the solution of lead is added to a boiling solution of the acid, no precipitate ensues, acid vapours are evolved, and the liquid becomes milky on cooling. In a short time, it deposits the new salt as a light, granular, white mass, which, under the microscope, appears to be made up of a multitude of spherical masses, which strongly refract light, and are of the size of human blood-corpuscles.

This salt is more easily soluble in an excess of the acetate than in water. It is easily soluble in spirit of wine, particularly in boiling spirit. Even in these solutions basic salts are easily formed. The addition of water to these solutions produces a precipitate.

The bibasic salts of lead and mercury, and the peculiar—perhaps acid—silver-salt, are subjects for further enquiry. The attempt to produce an acid baryta-salt, by evaporating two equal quantities of acid, one of which had been neutralized with carbonate, produced a mixture of neutral salt and leucic acid, having the form of a smeary, half-solid mass. That the neutral zinc-salt crystallizes from acid solutions, I have already stated.

The foregoing paper is the commencement of an enquiry into the nature and transformations of those amido-acids which play a part in the normal or abnormal chemical processes in man and animals.

Contributions to the History of the Phosphorus Bases.

By Augustus William Hofmann, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

THIRD MEMOIR.

Phosphammonium and Phospharsonium-, Diarsonium- and Arsammonium-Compounds.

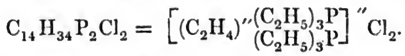
In the former section of this inquiry, I have endeavoured to trace the history of the bodies which are generated by the mutual action of triethylphosphine and dibromide of ethylene. Endeavouring, as far as possible, to fix with precision the several phases of this reaction, I have also carefully studied its principal products, the history of which appears to open the clearest perception of the nature of the polyatomic ammonias, and more especially of their connexion with the monatomic bases. The four saline compounds which, in accordance with the indications of theory, are formed by the action of dibromide of ethylene upon triethylphosphine, the bromides of the bromethylated, oxethylated, and vinylated monophosphonium, and of ethylene-diphosphonium, represent, in the phosphorus-series, as well as in the nitrogen and arsenic series, four classes of salts, the individual terms of which admit of being constructed in unlimited number and endless variety.

The following pages are devoted to the consideration of several compounds belonging to these four principal groups. The examination of the mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic- and arsenic-nitrogen-series, have more especially engaged my attention. Before, however, proceeding to a detailed account of these substances, which form more particularly the subject of this paper, a few experiments may still be briefly mentioned which are even more closely connected with the observations recorded in the previous memoir.

ACTION OF DICHLORIDE OF ETHYLENE ON TRIETHYLPHOSPHINE.

It is precisely analogous to that of dibromide of ethylene, giving rise to the two compounds—

$$C_8H_{19}PCl_2 = [(C_2H_4Cl)\ (C_2H_5)_3P]Cl, \text{ and}$$



$$C_{14}H_{34}P_2Cl_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2.$$

If the reaction be suffered to go on to the end under the influence of heat, the resulting white crystalline mass consists almost entirely of the diphosphonium-compound, no matter in what proportions the two bodies may be mixed, or whether they act upon one another in absence or in presence of alcohol or ether. To obtain the monatomic compound, a mixture of triethylphosphine with a very large excess of chloride of ethylene must be left to itself for some days. The white crystalline needles which the liquid deposits, are mixed even then with a considerable quantity of the diphosphonium-compound; but on treating their solution with dichloride of platinum, and leaving the pale-yellow precipitate, which exhibits an unmistakeable diphosphonic character, at rest for some hours, it becomes traversed by a number of deep orange-yellow crystalline stars, which may easily be separated from the yellow powder by mechanical rinsing. By boiling the yellow powder with water, an additional quantity of this orange-yellow salt is obtained, which may be purified, together with the first portion, by recrystallization. This salt resembles in most respects the platinum-salt of bromethylated triethylphosphonium; it is, however, somewhat more soluble, and exhibits a more decided tendency to assume the octohedral character. The properties of this body plainly show that it is the *platinum-salt of chlorethylated triethylphosphonium:*

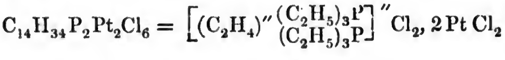
$$C_8H_{19}P\,Pt\,Cl_4 = [(C_2H_4Cl)(C_2H_5)_3P]Cl, Pt\,Cl_2.$$

The chloride prepared from the needle-shaped platinum-salt by sulphuretted hydrogen yielded, when treated with oxide of silver, a caustic liquid, which, after addition of hydrochloric acid and dichloride of platinum, deposited the well-known octohedra of the oxethylated phosphonium-salt:

$$[(C_2H_5O)(C_2H_5)_3P]Cl, Pt\,Cl_2.$$

No doubt could exist respecting the nature of the sparingly soluble diphosphonium-platinum-salt.

The formula



$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2, 2\,Pt\,Cl_2$$

was, nevertheless, established by experiment.

The compounds of chlorethylated triethylphosphonium are likewise formed under conditions similar to those which have already been mentioned as leading to the reproduction of the bromethylated from the oxethylated salt. On subjecting the chloride of oxethylated triethylphosphonium to the influence of pentachloride of phosphorus, a violent reaction takes place, attended with evolution of vapours of oxychloride of phosphorus. If the chloride of phosphorus be added by small portions till no further action is perceptible, and the mixture be then digested till the hydrochloric acid, the oxychloride, and any excess of pentachloride are driven off, the chloride of the chlorethylated compound remains in the retort.

$$[(C_2H_5O)\ (C_2H_5)_3P]\,Cl + P\,Cl_5 = PO\,Cl_3 + [(C_2H_4Cl)(C_2H_5)_3P]Cl + H\,Cl.$$

To fix the nature of this reaction by a number, the solution of the residual chloride was precipitated with dichloride of platinum. On recrystallizing the platinum-precipitate from boiling water, the beautiful needles characteristic of the chlorethylated compound immediately made their appearance, which on analysis were found to contain,

$$[(C_2H_4Cl)(C_2H_5)_3P]Cl,\ PtCl_2$$

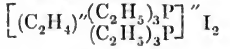
Monochlorinated chloride of ethyl acts on triethylphosphine like dichloride of ethylene. At the common temperature, and with a large excess of the chlorinated compound, the chloride of chlorethyl-triethylphosphonium is produced, which was easily identified by the reaction with excess of nitrate of silver and ammonia, repeatedly mentioned in the previous memoir. At the temperature of 100°, and with a considerable excess of triethylphosphine, crystals of the dichloride of ethylene-diphosphonium are soon deposited. The nature of the latter was fixed by the preparation of the characteristic platinum-salt, and of the beautifully crystallized di-iodide.

ACTION OF DI-IODIDE OF ETHYLENE ON TRIETHYLPHOSPHINE.

The two bodies, in the absence of solvents, act upon one another with explosive violence. The heat evolved causes the iodide of ethylene to resolve itself into ethylene and iodine, which unites directly with the phosphorus-base. If the violence of the action be diminished by admixture of alcohol, a white crystalline mass is obtained consisting almost entirely of the hydriodate of the phosphorus-base.

If the compounds

$$[(C_2H_4I)(C_2H_5)_3P]\,I \text{ and}$$



$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

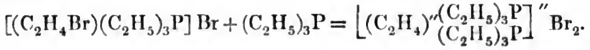
are likewise formed, they must be present in extremely small quantities only. The crystals, dissolved in water and decomposed by baryta, left, after the triethylphosphine had been removed by ether, the iodine by oxide of silver, and the baryta by means of carbonic acid, scarcely traces of an organic compound. The triethylphosphine evidently acts upon iodide of ethylene just like an alcoholic solution of potassa, the chief phase of the reaction doubtless consisting in the transformation:

$$(C_2H_5)_3P + (C_2H_4)I_2 = [(C_2H_5)_3HP]\,I + C_2H_3I.$$

I should not omit to mention, however, that the production of iodide of vinyl (C_2H_3I) was not demonstrated by a special experiment. There was some probability of an iodethylated triethylphosphonium-compound being formed by the action of iodide of phosphorus on the chloride or iodide of the oxethylated metal; but these bodies do not act on one another.

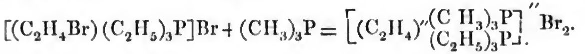
HYBRIDS OF ETHYLENE-DIPHOSPHONIUM.

In a former paragraph, I mentioned as a fact of peculiar interest, the formation of the dibromide of hexethylated ethylene-diphosphonium by the reaction



$$[(C_2H_4Br)(C_2H_5)_3P]\,Br + (C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

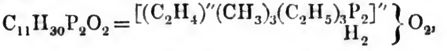
The study of this reaction naturally led me to try that of trimethylphosphine on the bromide of bromethylated triethylphosphonium, which I had a right to expect would thus be converted into the dibromide of ethylene-trimethyl-triethyldiphosphonium:



$$[(C_2H_4Br)\,(C_2H_5)_3P]Br + (CH_3)_3P = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

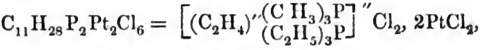
ACTION OF TRIMETHYLPHOSPHINE ON BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was, of course, examined only as far as necessary to establish the character of the reaction. The bromide of the hybrid diphosphonium is more soluble than the similar diphosphonium-compound previously described, which in other respects it greatly resembles. Oxide of silver eliminates the extremely caustic base,



$$C_{11}H_{30}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_3(C_2H_5)_3P_2]''\\H_2\end{matrix}\right\}O_2,$$

which yields with hydrochloric acid and dichloride of platinum, a pale-yellow platinum-salt,



$$C_{11}H_{28}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2,$$

crystallizing in scales from boiling water.

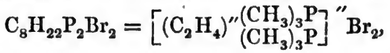
The salts of the hybrid diphosphonium crystallize like those of the corresponding hexethylated compound, but, as far as they have been examined, are somewhat more soluble; this remark applies especially to the di-iodide.

It seemed worth while to try whether the bromide of bromethylated triethylphosphonium was capable of fixing a molecule of *phosphoretted hydrogen*. I found, however, that the two bodies do not act upon one another. Phosphoretted hydrogen gas, passed through the alcoholic solution of the bromide, either cold or boiling, did not seem to affect it in any way.

ACTION OF DIBROMIDE OF ETHYLENE ON TRIMETHYLPHOSPHINE.

This reaction exhibits a repetition of all the phenomena observed in that which takes place between the dibromide and triethylphosphine. The process is completed, if possible, even sooner than in the ethyl-series. The lower boiling-point and overpowering odour of the trimethylphosphine render it advisable to mix the materials with considerable quantities of alcohol or ether; moreover, on account of the extreme oxidability of the phosphorus-compound, it is necessary to operate in vessels filled with carbonic acid and immediately sealed before the blowpipe. After digestion for a short time at 100°, the mixture of the two liquids solidifies to a hard, dazzling white, crystalline mass, containing the two bromides,

$$C_5H_{13}PBr_2 = [(C_2H_4Br)(CH_3)_3P]Br, \text{ and}$$



$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2,$$

one or the other predominating, according to the proportions in which the two bodies were allowed to act upon one another.

It is not difficult to establish by numbers the formation of these two bodies.

Bromide of Bromethyl-trimethylphosphonium.—When a solution of trimethylphosphine in absolute alcohol, mixed with a very large excess of dibromide of ethylene, is exposed for some hours to a temperature of from 50° to 60°, the liquid on cooling deposits well-formed crystals. It is desirable not to pass this temperature; at the boiling point of water the mixture turns brown, in consequence of secondary reactions. One or two crystallizations from absolute alcohol render the crystals perfectly pure; they exhibit in this state the chemical and physical characters of the corresponding ethylated body, possessing, however, a different crystalline form.

The formula is

$$C_5H_{13}PBr_2 = [(C_2H_4Br)(CH_3)_3P]Br.$$

Platinum-salt.—This is easily formed by treating the bromide with chloride of silver, when a crystallizable chloride is produced, which yields with dichloride of platinum splendid orange-yellow needles, containing

$$C_5H_{13}PBrPtCl_3 = [(C_2H_4Br)(CH_3)_3P],PtCl_2.$$

I have already mentioned that the bromide of bromethyl-trimethylphosphonium crystallizes differently from the bromide of the ethylated body. Whilst the latter is obtained in rhombic dodecahedrons, the methylated bromide affects forms belonging to the trimetric system. Quintino Sella has made the following examination of this compound:—

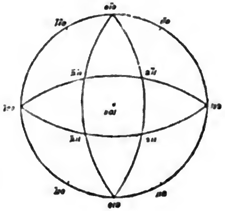
"System trimetric:—

100, 110 = 60° 24′;
001, 101 = 22° 9′.

Forms observed:—

100, 010, 001, 110, 211 (Fig. 54).

Fig. 54.*



Combinations observed:—

100, 010, 001; 110 (Fig. 55).
100, 010, 001; 110, 211 (Fig. 56).
110, 001; 100 (Fig. 57).
110, 001; 100, 010, 211 (Fig. 58).
001, 010, 211 (Fig. 59).

Fig. 55.

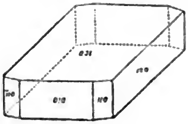
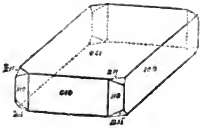


Fig. 56.



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* The figures are numbered consecutively with those in Dr. Hofmann's former paper on the Phosphorus Bases, Vol. XIV, p. 73.

Fig. 57.

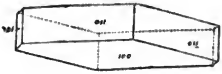


Fig. 58.

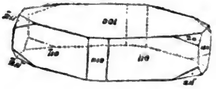
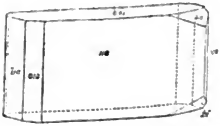


Fig. 59.

The crystals are generally tabular, as in the above figures; sometimes, however, they are elongated in the direction [001], and then the faces are most unequally developed. Figs. 60 and 61, and, again, Figs. 62 and 63 exhibit two very remarkable crystals of this kind.

Fig. 60.



The faces of the form 2 1 1 are generally very unequally developed, and some are actually wanting. In the crystals Figs. 60 and 61, and, again, Figs. 62 and 63, only two out of the eight faces 2 1 1 were well developed. The six others were wanting, or could but just be traced.

Fig. 61.

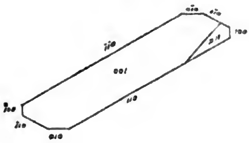


Fig. 62.

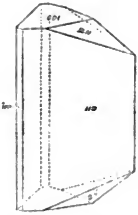
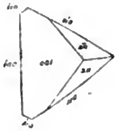


Fig. 63.



The lustre of the faces 0 0 1 is glassy, or even pearly. The lustre of the other faces is less marked, and more fatty.

Cleavages 0 0 1 easily obtained and rather perfect; 1 1 0 easily obtained, but fibrous.

The axes of optical elasticity, in the order of magnitude, are [0 0 1], [1 0 0], [0 1 0]."

Compounds of Oxethyl-trimethylphosphonium.

The liquid filtered from the sulphide of platinum, in the analyses of the platinum-salt of bromethyl-trimethylphosphonium, yielded by evaporation the extremely soluble and deliquescent chloride. This salt has not been analysed; but I have transformed it, by oxide of silver, into the corresponding oxethylated compound,

$$C_5H_{15}PO_2 = \left.\begin{matrix}[(C_2H_5O)\ (CH_3)_3P] \\ H\end{matrix}\right\} O.$$

The caustic liquid is converted by hydrochloric acid into the easily soluble chloride corresponding to the hydrate; this chloride, treated with dichloride of platinum, yields the platinum-salt of oxethylated trimethylphosphonium, which crystallizes in octohedra, like the corresponding ethyl-compound, but is distinguished from the latter by its extraordinary solubility in water. It was found to contain:

$$C_5H_{14}PO\,PtCl_3 = [(C_2H_5O)(CH_3)_3P]Cl, PtCl_2.$$

SALTS OF ETHYLENE-HEXMETHYL-DIPHOSPHONIUM.

Dibromide.—This salt is formed when dibromide of ethylene is treated with an excess of trimethylphosphine. The reaction is rapidly accomplished at the temperature of boiling water. The salt resembles the dibromide of the ethyl-series in its properties. It is extremely soluble, and was only once obtained in well-defined crystals, which were analysed and determined. Many efforts were made to produce these well-formed crystals a second time, but without success. Formula:

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)'' \begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]'' Br_2,$$

The following are the details of Sella's crystallographical determination:—

"System monoclinic:—

100, 101, = 17° 45′; 101, 001 = 20° 4′; 010, 111 = 57° 47′.

Fig. 64.

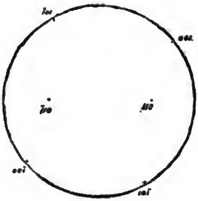
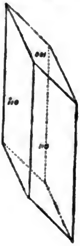


Fig. 65.



Forms observed:—

001, $\bar{1}$10, $\bar{1}$01 (Fig. 64).

Combinations observed:—

001, 110 (Fig. 65).

The face $\bar{1}\,0\,1$ has not been directly observed, but was found to be a cleavage. There is also another cleavage $0\,0\,1$, as distinct and easily obtained as $\bar{1}\,0\,1$."

The dibromide of hexmethylated ethylene-diphosphonium, treated with oxide of silver, yields the corresponding hydrate,

$$C_8H_{24}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_6P_2]''\\ H_2\end{matrix}\right\}O_2,$$

which forms with acids a series of salts resembling the corresponding ethyl-compounds. Of these I have briefly examined the di-iodide and the platinum-salt.

Di-iodide.—The base, neutralized with hydriodic acid, furnishes a salt crystallized in difficultly soluble needles, surpassing in beauty the corresponding body in the ethyl-series.

Formula:—

$$C_8H_{22}P_2I_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]' I_2,$$

Platinum-salt.—This is an apparently amorphous precipitate, which is nearly insoluble in water, dissolves with extreme slowness in boiling hydrochloric acid, and separates therefrom on cooling in golden-yellow laminæ, very much like those of the platinum-salt of the hybrid ethylene-trimethyl-triethyl-diphosphonium. It consists of

$$C_8H_{22}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Cl_2,2PtCl_2.$$

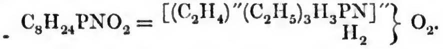
SERIES OF MIXED DIATOMIC BASES.

The investigation of the intimate relation which unites the bromethylated monophosphonium with the ethylene-diphosphonium-compounds, together with the establishment of the easy transition from the monatomic to the diatomic series, naturally suggested the idea of subjecting the bromethylated bromide, which forms the starting-point of the whole investigation, to the action of *monamines*, *monarsines*, and *monostibines*, in the expectation that diatomic bases would be formed containing nitrogen, arsenic, and antimony, side by side with phosphorus, and equivalent to it in chemical value and character. How far this expectation has been realized may be seen from the following experiments.

PHOSPHAMMONIUM-COMPOUNDS.

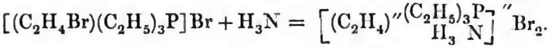
Action of Ammonia on Bromide of Bromethyl-triethylphosphonium.

In alcoholic solution, these two bodies act upon one another at ordinary temperatures, the reaction being indicated by considerable evolution of heat. To ensure complete transformation, the mixture is digested at 100° for half an hour in sealed tubes. On evaporating the alcohol and the excess of ammonia, there remains an extremely deliquescent saline mass, which crystallizes with difficulty. To remove small quantities of ammonia which may be present in the form of bromide of ammonium, the solution of the saline residue is treated with excess of oxide of silver, whereby a strongly alkaline liquid is set free, which may be digested on the water-bath without decomposition, so that traces of ammonia are easily driven off. Further investigation showed the presence in the caustic alkaline liquid of a base containing both phosphorus and nitrogen, viz. the hydrate of ethylene-triethylphosphammonium,



$$C_8H_{24}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3PN]'' \\ \hfill H_2\end{matrix}\right\} O_2.$$

The reaction between the bromethylated monophosphonium and ammonia had therefore taken place exactly as might have been expected from the behaviour of the former compound with the monophosphines:

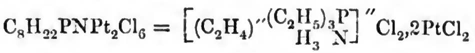


$$[(C_2H_4Br)(C_2H_5)_3P]Br + H_3N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3\ \ N\end{matrix}\right]'' Br_2.$$

I have fixed the composition of the nitrophosphoretted base by the analysis of the platinum-salt and of the gold-salt.

Platinum-salt.—On saturating the alkaline hydrate with hydrochloric acid and adding dichloride of platinum, a very voluminous, pale-yellow, slightly crystalline precipitate is obtained, which is difficultly soluble in boiling water, and also in boiling concentrated hydrochloric acid. The acid solution deposits well-formed prismatic crystals. The crystallization from concentrated hydrochloric acid is necessary to ensure the purity of the product; it appears that the direct precipitate contains an admixture which remains dissolved in the acid.

Analysis led to the formula



$$C_8H_{22}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3\ \ N\end{matrix}\right]'' Cl_2,2PtCl_2$$

Some of the crystals, obtained on slowly cooling a boiling solution in concentrated hydrochloric acid, were sufficiently well-formed to enable Q. Sella to examine them crystallographically. He has communicated to me the following description:—

"System trimetric:—

100, 110 = 59° 50′; 001, 101 = 70° 38′.

Forms observed:—

100, 110, 101. 010 (Fig. 66).

Fig. 66.

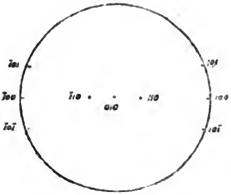


Fig. 67.

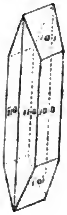
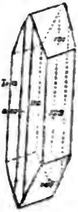


Fig. 68.



Combinations observed:—

100, 110, 101 (Fig. 67).
100, 110, 101; 010 (Fig. 68).

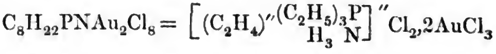
Cleavage 010 imperfect.

The faces 101 are dull, the others brilliant. The crystals are optically negative. The medium line is perpendicular to 100, and the plane of the optical axes is parallel to 001. The external angle of the optical axes appears to be about 60°.

Hardness greater than that of gypsum."

Gold-salt.—The solution of the dichloride, which is obtained by treating the crystallized platinum-salt with hydrosulphuric acid, yields with trichloride of gold a golden-yellow precipitate consisting of fine needles, which are difficultly soluble in water.

The formula of the salt is



$$C_8H_{22}PNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\ H_3\ N\end{matrix}\right]''Cl_2,2AuCl_3$$

The analyses of the platinum-salt and of the gold-salt sufficiently fix the composition of the series of diatomic phosphammonium-compounds. I have prepared some of the simple salts of this nitrophosphoretted metal, especially the dichloride, the dibromide, and the di-iodide. They all crystallize pretty well, although they are in general more soluble and less stable than the diphosphonium-salts. The diperchlorate is rather difficultly soluble, and crystallizes with facility. These salts have not been analyzed. The free base likewise resembles the hydrate of the diphosphonium. Its solution is powerfully alkaline, and precipitates from most metallic salts the hydrates of the metals. The solution of the base may be concentrated on the water-bath without losing ammonia; addition of potassa to the residuary liquid separates the hydrate in oily drops, which redissolve when mixed with water.

The peculiar construction of this body induced me to examine its deportment under the influence of heat. The substitution being limited to 5 equivs. of hydrogen, the question arose whether the hydrate could be distilled in the form of a phosphamine of the formula

$$\left.\begin{array}{l}(C_2H_4)''\\(C_2H_5)_2\\(C_2H_5)H\end{array}\right\}PN.$$

Experiment showed, however, that the base cannot be volatilized without entire decomposition; the product of distillation no longer contains a trace of the original body. Ammonia is abundantly evolved during the distillation, and at a certain stage of the process the residue contains the *hydrate of vinylated triethylphosphonium*,

$$\left.\begin{array}{r}[(C_2H_4)''(C_2H_5)_3H_3PN]''\\H_2\end{array}\right\}O_2 = H_3N + H_2O + \left.\begin{array}{r}[(C_2H_3)\ (C_2H_5)_3P]\\H\end{array}\right\}O.$$

I infer this from the analysis of an iodide obtained by neutralizing with hydriodic acid the mixed base which had been heated for some time. This salt was exceedingly soluble in water, and even in absolute alcohol; it was precipitated from the latter by addition of ether, and found to contain

$$C_8H_{18}PI = [(C_2H_3)\ (C_2H_5)_3P]I.$$

The mother-liquor of this salt was freed from excess of silver and precipitated by trichloride of gold. The yellow needles thus obtained were found to be the corresponding gold-salt

$$C_8H_{18}PAuCl_4 = [(C_2H_3)\ (C_2H_5)_3P]Cl, AuCl_3$$

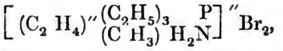
The deportment of the bromethylated bromide under the influence of ammonia, opens an almost unlimited series of diatomic nitrophosphoretted metals. It is only necessary to replace in the above reaction the ammonia by a monamine, in order to obtain a new metal of almost any composition that could be desired. I have produced a few bodies of this description, in order to establish experimentally the relations, which theory, resting on the observations in the ammonia-reaction, sufficiently suggests.

ACTION OF METHYLAMINE ON THE BROMIDE OF BROMETHYLTRIETHYLPHOSPHONIUM.

COMPOUNDS OF ETHYLENE-METHYL-TRIETHYLPHOSPHAMMONIUM.

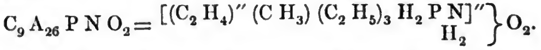
Repetition of all the phenomena observed in the experiment with ammonia. Both substances unite on digestion,

$$[(C_2\,H_4\,Br)\,(C_2\,H_5)_3\,P]\,Br + (C\,H_3)\,H_2\,N =$$



$$\left[(C_2\,H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (C\,H_3)\,H_2 & N\end{matrix}\right]''Br_2,$$

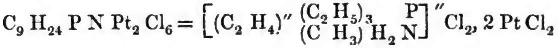
and the compound yields, on treatment with oxide of silver, the caustic base



$$C_9\,A_{26}\,P\,N\,O_2 = \left.\begin{matrix}[(C_2\,H_4)''\,(C\,H_3)\,(C_2\,H_5)_3\,H_2\,P\,N]''\\ H_2\end{matrix}\right\}O_2.$$

I have been satisfied to fix the composition of this body by the analysis of a rather difficultly soluble platinum-compound, crystallizing from boiling water in splendid needles, frequently an inch in length. I did not succeed, however, in obtaining, either from boiling water, or from boiling hydrochloric acid, crystals which could have been determined.

Formula:



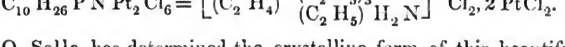
$$C_9\,H_{24}\,P\,N\,Pt_2\,Cl_6 = \left[(C_2\,H_4)''\begin{matrix}(C_2\,H_5)_3 & P\\ (C\,H_3)\,H_2 & N\end{matrix}\right]''Cl_2,\,2\,Pt\,Cl_2$$

ACTION OF ETHYLAMINE ON THE BROMIDE OF BROMETHYLTRIETHYLPHOSPHONIUM.

COMPOUNDS OF ETHYLENE-TETRETHYLPHOSPHAMMONIUM.

The two bodies unite with evolution of heat. Since the salts of the new phosphammonium crystallize very beautifully, I have not been able to resist the temptation of examining several of them somewhat more minutely.

Platinum-salt.—The crude product of the reaction, purified with oxide of silver and saturated with hydrochloric acid, furnishes, on addition of dichloride of platinum, an orange-yellow platinum-compound, crystallizing in needles very similar to those of the methyl-compound above-described. The salt, recrystallized from boiling water, has the composition



$$C_{10}\,H_{26}\,P\,N\,Pt_2\,Cl_6 = \left[(C_2\,H_4)''\begin{matrix}(C_2\,H_5)_3 & P\\ (C_2\,H_5)\,H_2 & N\end{matrix}\right]''Cl_2,\,2\,PtCl_2.$$

Q. Sella has determined the crystalline form of this beautiful salt.

"System monoclinic:—

100, 101 = 43° 35′; 101, 001 = 43° 17′; 111, 010 = 55° 36′.

Forms observed:—

100, 001, 110, 011 (Fig. 69).

Combinations observed:—

110, 011 (Fig. 70).
110, 011, 001 (Fig. 71).
110, 011, 001, 100 (Figs. 72, 73).

Fig. 69.

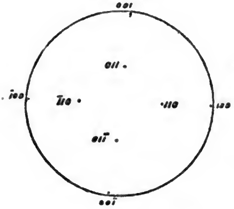


Fig. 70.

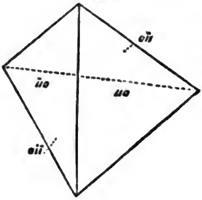


Fig. 71.

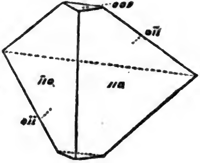


Fig. 72.

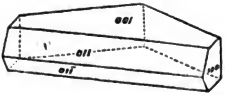
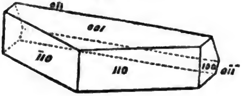


Fig. 73.



The crystals are hemihedral: the faces 0 0 1 and 1 0 0 have their parallels, but of the four faces of the forms 1 1 0 and 0 1 1 only two were observed with their corresponding parallels.

All the crystals examined exhibit the faces 1 1 0, $\bar{1}$ 1 0, and the faces 0 $\bar{1}$ 1, 0 $\bar{1}$ $\bar{1}$ (Figs. 70, 71, and 73). In a single crystal (Fig. 72) the faces $\bar{1}$ $\bar{1}$ 0, 1 $\bar{1}$ 0, and the faces 0 1 1, 0 1 $\bar{1}$ were observed. It is evident that the crystals Figs. 72 and 73 are symmetrical but not superposible.

The crystals frequently exhibit the habitus of triangular tables (Figs. 72 and 73); sometimes they are tetrahedrons (Fig. 70), or bevelled tetrahedrons (Fig. 71).

The faces are very brilliant but very often rounded, so that they are apt to yield many images and a great difference in the angles.

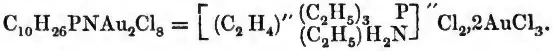
The plane of polarization is not altered if the light passes through the faces 0 0 1, 0 0 $\bar{1}$ and the faces 1 0 0, $\bar{1}$ 0 0 in the direction [0 1 0].

Colour orange-red.

The minuteness of the crystals, and the difficulty of fixing them on account of their hemihedral form, has prevented me from finding their cleavages."

Gold-salt.—Golden-yellow, difficultly soluble needles, which may be recrystallized from boiling water without decomposition.

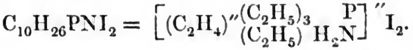
Analysis led to the formula



$$C_{10}H_{26}PNAu_2Cl_8 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]'' Cl_2,2AuCl_3.$$

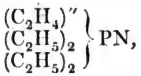
Di-iodide.—It was prepared from the recrystallized platinum-salt by treatment with sulphuretted hydrogen, decomposition of the resulting dichloride by oxide of silver, and neutralization of the liberated base with hydriodic acid. White acicular crystals, extremely soluble in water, but not deliquescent, likewise very soluble in spirit of wine, difficultly soluble in absolute alcohol, insoluble in ether. From the alcoholic liquid, the salt is precipitated by ether in the crystalline state. From the aqueous solution, the iodide separates, on addition of potassa, in the form of oily globules, which gradually solidify with crystalline structure.

Formula:



$$C_{10}H_{26}PNI_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5) & H_2N\end{matrix}\right]'' I_2.$$

The caustic base, which corresponds to the iodide, is readily obtained by oxide of silver. It presents considerable stability, and may be evaporated on the water-bath until it separates in heavy oily globules. Here again the action of heat might have given rise to the formation of a volatile phosphamine



$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)_2\\ (C_2H_5)_2\end{matrix}\right\} PN,$$

capable of reproducing the salts from which it was derived. But, exactly as in the case of the compound formed by the coalescence of triethylphosphine and ammonia, distillation destroys the base. The deportment of this substance under the influence of heat is characteristic; its study cannot fail to assist in the general elucidation of the constitution of this class of bodies. I may, in a subsequent inquiry, find an opportunity of returning to this question.

Both methylamine and ethylamine being primary monamines, I have, in conclusion, submitted the bromethylated bromide to the action of a secondary base, viz. diethylamine, and lastly, of some tertiary bases, viz. trimethylamine and triethylamine.

ACTION OF DIETHYLAMINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

COMPOUNDS OF ETHYLENE-PENTETHYLPHOSPHAMMONIUM.

The reaction is similar to that of ethylamine; the resulting product conveniently treated, yields a splendid platinum-salt crystallizing in rectangular plates, which contain

$$C_{12}H_{30}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\ \ P\\(C_2H_5)_2HN\end{matrix}\right]'' Cl, 2PtCl_2.$$

ACTION OF TRIMETHYLAMINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

ETHYLENE-TRIMETHYL-TRIETHYLPHOSPHAMMONIUM-COMPOUNDS.

As to the preparation and properties, I may refer to the preceding paragraphs. The platinum-salt crystallizes in beautiful needles, of the composition,

$$C_{11}H_{28}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3N\end{matrix}\right]'' Cl_2, 2PtCl_2.$$

The examination of this compound has induced me to perform an experiment which may here be briefly mentioned. The action of trimethylamine on dibromide of ethylene gives rise to the formation of a beautifully crystallized salt, the bromide of bromethyl-trimethylammonium, of which I have already published a slight sketch in the 'Proceedings of the Royal Society'.* I was curious to ascertain whether the dibromide, generated by the union of *trimethylamine* with the bromide of bromethyl-*triethyl-phosphonium*, could likewise be formed by submitting the bromide of bromethyl-*trimethylammonium* to the action of *triethylphosphine*:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3N = [(C_2H_4Br)(CH_3)_3N]Br +$$
$$(C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3\ N\end{matrix}\right]'' Br_2.$$

The bromide of bromethylated trimethylammonium is indeed readily attacked by triethylphosphine, but the change is very different from what I had expected. I intend in another paper to return to the products of this reaction.

Before leaving the history of the phosphammonium-compounds, I have briefly to allude to a peculiar deportment of the bromethylated bromide. When treating this compound with triethylamine, instead of trimethylamine, expecting, of course, to observe a repetition of the phenomena so frequently witnessed, I was surprised to find that these substances, although acting with considerable energy, failed to produce the anticipated phosphammonium-compound. This unforeseen result induced me to examine this reaction repeatedly and with particular care. The result remained the same. On evaporating the alcoholic product of the reaction, and treating the concentrated solution with oxide of silver, a powerfully alkaline liquid remained, even after the expulsion of the triethylamine, considerable quantities of which were liberated. This residuary alkaline liquid, saturated with hydrochloric acid, yielded, on addition of dichloride of platinum, the beautiful octohedra of the oxethylated triethylphosphonium-platinum-salt, which was identified by analysis.

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* Proceedings of the Royal Society, vol. ix, p. 293.

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N + H_2O = \\ [(C_2H_5O)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

This equation involves the intervention of water in the reaction, which was obviously furnished by the imperfectly de-hydrated alcohol used in the experiments. In the anhydrous state, the bromethylated bromide and triethylamine scarcely act at 100°; between 120° and 130°, a reaction takes place, among the products of which, as yet very imperfectly examined, I was likewise unable to trace the presence of a phosphammonium-like-compound. It can scarcely be doubted that this reaction gives rise to the formation of bromide of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N = [(C_2H_3)(C_2H_5)_3P]Br + \\ [(C_2H_5)_3HN]Br.$$

Experimentally the question remains undecided.

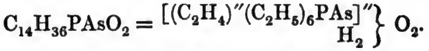
The elegance and precision with which the bromethylated bromide fixes the elements of ammonia and of the monamines, very naturally suggested the idea of examining the deportment of this body under the influence of diamines and triamines. The results obtained in these experiments do not belong to this part of the inquiry. Suffice it to say for the present, that these substances attack the bromide with the utmost energy, giving rise to an almost unlimited number of polyatomic bases of a higher order, the constitution of which, though complicated, is traceable in advance by the experience acquired in the simpler forms of reaction.

PHOSPHARSONIUM-COMPOUNDS.

There was no necessity for entering into a detailed examination of this class of compounds. I have in fact been satisfied to establish, by a few characteristic numbers, the existence of the phospharsonium-group.

ACTION OF TRIETHYLARSINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

On digesting the two substances in sealed tubes, the usual phenomena are observed. The saline mass which is formed yields, by treatment with oxide of silver *in the cold,* a powerfully alkaline solution, containing the *dihydrate of ethylene-hexethylphospharsonium,*



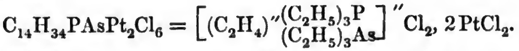
$$C_{14}H_{36}PAsO_2 = \left.\begin{matrix}[(C_2H_4)^{\prime\prime}(C_2H_5)_6PAs]^{\prime\prime} \\ H_2\end{matrix}\right\} O_2.$$

It is thus obvious that arsenic-base imitates triethylphosphine in its deportment with the bromethylated bromide. The two substances simply combine to form the dibromide of the phospharsonium.

The alkaline solution of the hydrate of the phospharsonium exhibits the leading characters of this class of bases; I may therefore refer to the detailed account which I have given of the hydrate of the diphosphonium. The saline compounds likewise resemble those of the diphosphonium. The dichloride and the di-iodide were obtained in beautiful crystalline needles, exhibiting a marked tendency to form well-crystallized double salts. I have prepared the compounds of the dichloride with chloride of tin, bromide of zinc, trichloride of gold, and lastly, with dichloride of platinum. The latter compound was analysed in order to fix the composition of the series.

Platinum-salt.—The product of the reaction of triethylarsine upon the bromethylated bromide is treated with oxide of silver *in the cold,* and the alkaline solution thus obtained is saturated with hydrochloric acid, and precipitated with dichloride of platinum. An exceedingly pale yellowish, apparently amorphous precipitate of marked diphosphonic appearance is thrown down, almost insoluble in water, but dissolving in boiling concentrated hydrochloric acid. The hydrochloric solution deposits, on cooling, beautiful orange-red prisms, resembling the crystals of the corresponding diphosphonium-platinum-salt.

Formula:



$$C_{14}H_{34}PAsPt_2Cl_6 = \left[(C_2H_4)^{\prime\prime}\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3As\end{matrix}\right]^{\prime\prime} Cl_2,\ 2PtCl_2.$$

Quintino Sella has examined the crystals of the phospharsonium-platinum-salt. I append the results of his observations.

"System triclinic :—

100, 010 = 81° 52′; 100, 001 = 88° 14′;
010, 001 = 89° 9′; 100, $\bar{1}11$ = 120° 18′;
010, $\bar{1}11$ = 61° 4′.

Forms observed:—

$100,\ 001,\ 010,\ 011,\ \bar{1}11,\ 02\bar{1}$ (Fig. 74).

Combinations:—

$100,\ 010,\ 001$ (Fig. 75).
$100,\ 010,\ 001;\ \bar{1}11$ (Fig. 76).
$100,\ 010,\ 001;\ \bar{1}11,\ 02\bar{1}$
$100,\ 010,\ 001;\ \bar{1}11,\ 02\bar{1},\ 011$ (Fig. 77).

Fig. 74.

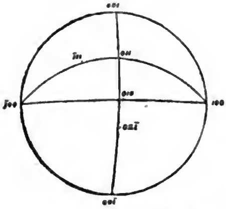


Fig. 75.

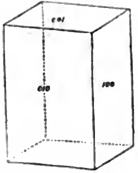


Fig. 76.

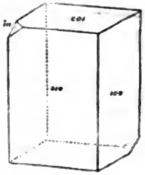


Fig. 77.

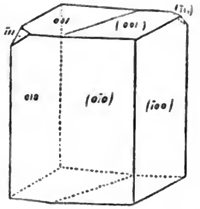
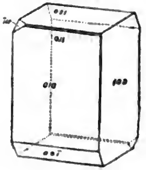


Fig. 78.



Cleavages 100 and 001: distinct and easily obtained. The cleavage is occasionally observed to take place during measuring, probably in consequence of the heat emanating from the face, which has to be brought close on account of the minuteness of the crystals.

Hemitropic crystals with the axis of hemitropy [0 0 1] (Fig. 78). It was possible to verify by measurement that the axis of hemitropy is really [0 0 1], and not a line perpendicular to one of the faces of the crystal."

The phospharsonium-compounds, and more especially the hydrate of the series, are far less stable than the corresponding terms of the diphosphonium-series.

If the product of the action of triethylarsine on the bromethylated monophosphonium be *boiled* with oxide of silver, instead of being treated in the cold, not a trace of the phospharsonium-compound is obtained. The caustic solution which is formed, yields, when saturated with hydrochloric acid and precipitated with dichloride of platinum, only the rather soluble octohedral crystals of the oxethylated triethylphosphonium. The nature of this transformation is clearly exhibited when a solution of the hydrate of the phospharsonium, filtered off *in the cold* from the excess of oxide of silver, is submitted to ebullition. Immediately the clear liquid is rendered turbid from separated triethylarsine, which becomes perceptible, moreover, by its powerful odour; the solution now contains the hydrate of oxethylated triethylphosphonium.

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3As + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O$$

When the dibromide is boiled with the oxide of silver, a beautiful silver mirror is formed on the sides of the vessel, obviously in consequence of a partial oxidation of the liberated triethylarsine.

Some experiments were made to produce a diatomic compound containing phosphorus and antimony. I expected to form this body, the dibromide of a phosphostibonium, by the action of triethylstibine on the bromethylated bromide, so frequently mentioned in this paper. The two bodies react upon one another, but only after protracted digestion or exposure to a rather high temperature. The product of the reaction is complex, yielding a comparatively small quantity of a difficultly soluble platinum-salt of diatomic appearance. I have repeatedly modified the reaction, and analysed the products in the form of platinum-salts; I omit to quote the detail of these experiments, since they have failed to disentangle the difficulties of the reaction.

Some experiments upon the deportment of dibromide of ethylene with triethylarsine were more successful. The reaction between these two bodies had been selected as a subject of inquiry by Mr. W. Valentin, to whom I am indebted for valuable assistance in the earlier stages of these researches. Circumstances have subsequently prevented Mr. Valentin from carrying out his plan, and I have therefore to take upon myself the responsibility for the following statements. The results obtained in the examination of the arsenic-compounds are by no means absolutely connected with the study of the phosphorus-bases; nevertheless I may be permitted to lay them before the Society, together with the account of the corresponding reaction in the phosphorus-series.

MONARSONIUM-COMPOUNDS.

ACTION OF DIBROMIDE OF ETHYLENE UPON TRIETHYLARSINE.

The experience gathered during the examination of the phosphorus-bodies enabled me to establish the nature of this reaction by a comparatively small number of platinum-determinations.

Bromide of Bromethyl-triethylarsonium.—To avoid, as far as possible, the formation of the second product, a mixture of triethylarsine with a very large excess of dibromide of ethylene was digested in sealed tubes, at a temperature not exceeding 50° C. Notwithstanding this low temperature, the tubes invariably contained compressed gases. The product of the reaction was treated with water, which extracted a soluble bromide from the ethylene-compound unacted upon. On evaporation, a beautiful bromide was left, which, being copiously soluble in boiling, and sparingly soluble in cold alcohol, could be readily recrystallized from absolute and even from common alcohol. In water this substance is excessively soluble; it is, therefore, scarcely crystallizable from an aqueous solution.

Analysis, as might have been expected, proved this salt to be the analogue of the bromethylated triethylphosphonium-salt. It contains

$$C_8H_{19}AsBr_2 = [(C_2H_4Br)(C_2H_5)_3As]Br.$$

The bromide of bromethyl-triethylarsonium can be obtained in beautiful crystals. Their form—the rhombic dodecahedron—is identical with that of the corresponding bromethyl-triethylphosphonium-compound, which the crystals resemble also in their general habitus. They were measured by Q. Sella.

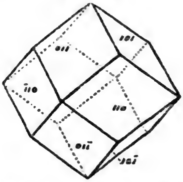


Fig. 79.

"System monometric.

Forms observed:—

110 (Fig. 79).

No influence on polarized light."

Platinum-salt.—The solution of the previous salt, converted by treatment with chloride of silver into the corresponding chloride, yields with dichloride of platinum splendid needles of a double salt, difficultly soluble in cold and even in boiling water, containing—

$$C_8H_{19}BrAsPtCl_3 = [(C_2H_4Br)(C_2H_5)_3As]Cl,PtCl_2.$$

COMPOUNDS OF VINYL-TRIETHYLARSONIUM.

The bromide of bromethyl-triethylarsonium, like the corresponding phosphorus-compound, loses its latent bromine under the influence of oxide of silver. If the solution of the bromide be precipitated by an excess of nitrate of silver, one-half of the bromide separates as bromide of silver; the clear filtrate, mixed with ammonia, yields the second half of the bromine in the form of a dense precipitate. Nevertheless the reaction differs from that observed in the phosphorus-series. The bromide of the bromethylated phosphonium, as has been pointed out in a former part of this inquiry, is almost invariably converted into an oxethylated body, its transformation into a vinyl-compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields, as a rule, the vinyl-body of the series, the formation of an oxethylated compound taking place only under particular circumstances; in fact so rarely as to leave some doubt regarding the existence of this term of the series. The bromide of the bromethylated arsonium, treated with an excess of oxide of silver, yields a powerfully alkaline solution, the nature of which was determined by the analysis of the corresponding platinum-salt. Transformed into the chloride, and precipitated by dichloride of platinum, this solution yielded beautiful rather soluble octohedra of the formula:

$$C_8\,H_{18}\,As\,Pt\,Cl_3 = [(C_2\,H_3)\ (C_2\,H_5)_3\,As]\,Cl,\,Pt\,Cl_2.$$

Gold-salt.—The chloride obtained in the analysis of the platinum-salt, gives with trichloride of gold a yellow, difficultly soluble, faintly crystalline precipitate of the formula:

$$C_8\,H_{18}\,As\,Au\,Cl_4 = [(C_2\,H_3)\ (C_2\,H_5)_3\,As]\,Cl,\,Au\,Cl_3.$$

These results show that the transformation of the bromethylated compound ensues according to the following equation:—

$$[(C_2\,H_4\,Br)\ (C_2\,H_5)_3\,As]\,Br + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O = 2\,Ag\,Br + \left.\begin{matrix}[(C_2\,H_3)(C_2\,H_5)_3\,As]\\H\end{matrix}\right\}O.$$

The idea suggested itself that the vinyl-compound obtained in this reaction might be a secondary product resulting from the decomposition of an oxethylated compound of limited stability formed in the first instance:—

$$\left.\begin{matrix}[(C_2\,H_5\,O)\ (C_2\,H_5)_3\,As]\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2\,H_3)\ (C_2\,H_5)_3\,As]\\H\end{matrix}\right\}O.$$

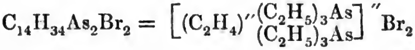
It was with the view of avoiding this decomposition, that in some of the experiments, the digestion was accomplished at the common temperature; the result, however, showed that even in these cases the vinyl-compound was obtained.

Nevertheless the oxethylated body appears to exist. Under circumstances which were not sufficiently well observed at the time, the action of oxide of silver upon the bromide of the bromethylated triethylarsonium yielded an octohedral platinum-salt with the platinum percentage of the oxethylated compound:

$$[(C_2H_5O)(C_2H_5)_3As]Cl, PtCl_2.$$

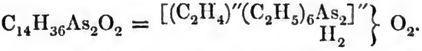
DIARSONIUM-COMPOUNDS.

Dibromide of Ethylene-hexethyl-diarsonium.—The bromide or chloride of the bromethylated arsonium is but slowly acted upon by triethylarsine at 100° C. Two days' digestion at that temperature had produced but a slight impression; at 150° the reaction is accomplished in two hours. The phenomena now to be recorded presented themselves in the succession repeatedly observed in the phosphorus-series. The dibromide



$$C_{14}H_{34}As_2Br_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$$

yielded, when debrominated, the powerful alkali

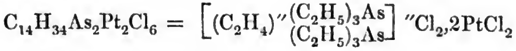


$$C_{14}H_{36}As_2O_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6As_2]''\\H_2\end{matrix}\right\}O_2.$$

Treated with acids, this alkali produces a series of fine salts, amongst which the di-iodide deserves to be mentioned; it equals in beauty the corresponding diphosphonium-compound. I have fixed the composition of the series by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Pale yellow crystalline precipitate, similar to the diphosphonium-compound, difficultly soluble in water, soluble in boiling concentrated hydrochloric acid, from which it crystallizes on cooling.

Formula:



$$C_{14}H_{34}As_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Cl_2,2PtCl_2$$

Gold-salt.—The dichloride obtained after separating the platinum in the analysis of the platinum-salt by means of sulphuretted hydrogen, was precipitated by trichloride of gold. Yellow slightly crystalline precipitate, soluble in hydrochloric acid, from which it separates in golden-coloured plates of the composition,

$$C_{14}H_{34}As_2Au_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Cl_2,2AuCl_3$$

ARSAMMONIUM-COMPOUNDS.

Bromide of bromethylated triethylarsonium, as might have been expected, is capable of fixing ammonia and the monamines, giving rise to the formation of a series of compounds not less numerous than that of the bodies mentioned in the phosphammonium-series. I have been satisfied to study the action of ammonia upon the bromide.

Dibromide of Ethylene-triethylarsammonium.—Reaction complete in two hours at 100°.

The product contained the bromide

$$C_8H_{22}AsNBr_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\H_3 & N\end{matrix}\right]''Br_2.$$

which was converted, by means of oxide of silver, into the stable caustic base

$$C_8H_{24}AsNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3AsN]''\\H_2\end{matrix}\right\}O_2,$$

the composition of this base which was determined by the analysis of the platinum- and gold-salts.

Platinum-salt.—Needles difficultly soluble in boiling water, soluble in boiling concentrated hydrochloric acid, from which well-formed crystals are deposited.

Formula:

$$C_8H_{22}AsNPt_2Cl_6 = \left[C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\H_3 & N\end{matrix}\right]''Cl_2,2PtCl_2,$$

Gold-salt.—Yellow compound precipitated from the dichloride obtained in the analysis of the platinum-salt, on adding a solution of trichloride of gold. Soluble in hydrochloric acid; deposited from this solution in golden-yellow plates, containing

$$C_8H_{22}AsNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\H_3 & N\end{matrix}\right]''Cl_2,2AuCl_3$$

I have also made a few experiments on the action of dibromide of ethylene upon triethylstibine. The reaction is slow, and required long-continued digestion at temperatures higher than that of boiling water. The tubes invariably contained much gas, and the product of the reaction proved to be an inattractively complex mixture of several compounds, many of them secondary, which by no means invited me to a more minute examination of this process. I omit to quote the few platinum- and chlorine-determinations which were made, since they do not admit of a simple interpretation.

In performing the experiments on the arsenic-bases I have been most ably assisted by my nephew, Dr. P. W. Hofmann, to whom I express my best thanks for his active co-operation in this part of my inquiries.

The experiments carried out in the ethylene-series, develope clearly enough the nature of the diatomic bases, and their relation to the monatomic compounds. I have worked with predilection in this series, because the accesibility and manageableness of the material greatly facilitate the unravelling of the often complicated reactions. There could be no doubt that the phenomena observed in the ethylene-series would likewise be reproduced in other homologous series. But as a general view of the nature of this group of bodies had been gained from the observations recorded in the preceding paragraphs, it appeared scarcely necessary to corroborate the results already obtained, by many further experiments, which would have been more or less mere repetitions of the former. Nevertheless I have, in certain cases, drawn other groups into the circle of my observations. Some of the fragmentary results at which I thus arrived I will here briefly communicate.

METHYLENE-GROUP.

In another place* I have mentioned an experiment made in the hope of converting iodoform into iodide of carbon, which, however, yielded nothing but the di-iodide of methylene, discovered not long previously by Boutlerow. As a considerable quantity of this interesting compound (the result of these experiments) was still at my disposal, I took the opportunity of examining more particularly its behaviour to triethylphosphine and the ammonias in general.

The methylenated derivatives of the phosphorus-bases will be more conveniently examined in connexion with another class of compounds, to which a special chapter of this inquiry must be devoted. I will therefore only briefly mention in this place, that I have succeeded in producing several of the bases belonging to the methylene-group. The members of this series present some peculiarities, distinguishing them in a marked manner from the corresponding ethylene-compounds.

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* Journal of the Chemical Society, vol. xiii, p. 65.

PROPYLENE AND AMYLENE-GROUPS.

The experiments in the propylene- and amylene-groups were instituted almost at the beginning of this investigation, at a time when the reaction between triethylphosphine and dibromide of ethylene had not yet been sufficiently disentangled. The removal of the difficulties in the ethylene series has naturally cooled my interest in the corresponding reactions of the propylene- and amylene-series, and hence this part of the investigation has been left incomplete.

Triethylphosphine is briskly attacked by the dibromides, both of propylene and amylene; the reactions, however, do not exhibit the welcome simplicity and smoothness which characterize those in the ethylene-series. Even in the propylene-compound, whether it be prepared from amylic alcohol or from iodide of allyl, we miss with regret the sharply defined characters of the corresponding ethylene-body; and in the butylene-, and still more in the amylene-series, these features become fainter and fainter.

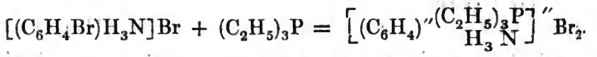
When submitted to the action of the dibromides of propylene and amylene, triethylphosphine appears to undergo simultaneously two different sets of changes, the substances formed being partly direct products of the reaction, partly and perhaps chiefly, indirect products. The diphosphonium-compounds of the propylene- and amylene-series are less stable than the ethylene-diphosphoniums, and are therefore always mixed with such products of decomposition as are formed in the ethylene-group only under the protracted influence of high temperatures. Under all circumstances, however, these dibromides give up the elements of hydrobromic acid, so that we have to eliminate a painfully small quantity of the searched-for products from an unprofitable mass of bromide of triethylphosphonium. In such cases the ordinary methods of separation no longer suffice, and we are compelled to resort to treatment with baryta, the real examination of the products beginning only after the liberated phosphorus-base has been removed by ether, and the bromide of barium decomposed by means of oxide of silver and carbonic acid. By this treatment, beautiful iodides and platinum-salts are obtained, which, however, have as yet been but partially and imperfectly investigated.

PHENYLENE-GROUP.

Unfortunately nothing but fruitless experiments. I had hoped to find in triethylphosphine a bridge between the phenyl- and the phenylene-series, but my expectations have not been realized. The analogy between the salts of bromethylated triethylphosphonium and of bromophenylated ammonium

$$\begin{array}{l}[(C_2H_4Br)\ (C_2H_5)_3P\,]Br,\\ [(C_6H_4Br)\quad\ \ H_3\ \ N]Br,\end{array}$$

is unmistakeable, and it remained to be seen whether triethylphosphine would attack the salts of bromophenylammonium according to the equation



$$[(C_6H_4Br)H_3N]Br + (C_2H_5)_3P = \left[(C_6H_4)''\begin{matrix}(C_2H_5)_3P\\ H_3\ N\end{matrix}\right]''Br_2.$$

Unfortunately the mixture of the two bodies is not changed even after being heated for some time to 160°. No better result was obtained by substituting for the bromophenylamine, the corresponding iodinated base. A mixture of triethylphosphine and iodophenylamine, which had been kept for a day at 160°, yielded, on opening the tube, an appreciable quantity of iodine, recognizable by silver-salts, but the decomposition was by no means complete. Hydriodic acid separated from the mixture an iodide which crystallized in long needles, and was found by analysis to consist of iodide of iodophenylammonium. In the products of transformation of the phosphorus-base I was unable to trace the simple relations pointed out by theory.

Benzylene-Group.

In conclusion, I will mention a few experiments upon the mutual reaction between triethylphosphine and dichloride of benzylene. By this latter name I denote the compound, discovered by Cahours, which is produced by the action of pentachloride of phosphorus on bitter almond oil.

At ordinary temperatures, and even at 100°, the two compounds react but slowly upon each other; between 120° and 130°, however, especially in presence of alcohol, the change takes place with facility. The resulting crystalline mass, like that obtained in the corresponding experiments in the propylene- and amylene-series, consists chiefly of chloride of triethylphosphonium. After removing the phosphorus-base as completely as possible from the solution of the crystals, by the successive treatment with baryta, oxide of silver, and carbonic acid, there remained a strongly alkaline liquid, the nature of which I endeavoured to determine by the preparation of the iodide and platinum-salt. The liquid, saturated with hydriodic acid, yielded a well-crystallized iodide, which, however, was so soluble and deliquescent that no constant results could be obtained by its analysis. On the other hand, the somewhat sparingly soluble platinum-salt, which is precipitated in small laminæ, on treating the solution of the chloride with dichloride of platinum, and may be recrystallized without alteration from boiling water, yielded results agreeing with one another, although the products of different preparations were submitted to analysis.

These analyses led to the formula

$$C_{13}H_{22}P\ PtCl_3 = [(C_2H_5)_3(C_7H_7)P]Cl, PtCl_2.$$

The transformation of triethylphosphine under the influence of dichloride of benzylene, evidently takes place according to the following equation:

$$3[(C_2H_5)_3P] + C_7H_6Cl_2 + H_2O = [(C_2H_5)_3HP]Cl + [(C_2H_5)_3(C_7H_7)P]Cl + (C_2H_5)_3PO.$$

It may be that the formation of the triethyl-benzylphosphonium-compound is preceded by the production of an ephemeral diatomic base containing the radical C_7H_6,

$$2[(C_2H_5)_3P] + C_7H_6Cl_2 = \left[(C_7H_6)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2,$$

which is subsequently decomposed under the joint influence of water and an excess of triethylphosphine. I have not, however, been able, experimentally, to trace this base. Moreover, a difference in the deportment of triethylphosphine with the compounds of ethylene and benzylene is readily intelligible, if we recollect that they are far from being analogous, dichloride of benzylene representing in the benzyl-group the diatomic derivatives which have been obtained from ethylic aldehyde.

The analysis of the benzyl-triethylphosphonium-platinum-salt concludes the experimental part of this section of my researches.

The following Table exhibits at a glance the several groups of bodies examined in Parts II. and III. of this inquiry.

Monatomic-Compounds. Phosphorus-Group.

Monophosphonium-salts. Ethyl-series.

Salt of Tetrethylphosphonium .	$[(C_2H_5)_4P]Br$.
Salt of Bromethyl-triethylphosphonium	$[(C_2H_4Br)\ (C_2H_5)_3P]Br$.
Salt of Chlorethyl-triethylphosphonium	$[(C_2H_4Cl)\ (C_2H_5)_3P]Br$.
Salt of Oxethyl-triethylphosphonium	$[(C_2H_4HO)\ (C_2H_5)_3P]Br$.
Salt of Vinyl-triethylphosphonium .	$[(C_2H_3)\ (C_2H_5)_3P]Br$.

Ethyl-methyl-series.

Salt of Ethyl-trimethylphosphonium	$[(C_2H_5)\ (CH_3)_3P]Br$.
Salt of Bromethyl-trimethylphosphonium	$[(C_2H_4Br)(CH_3)_3P]Br$.
Salt of Oxethyl-trimethylphosphonium	$[(C_2H_4HO)\ (CH_3)_3P]Br$.

Ethyl-benzyl-series.

Salt of Triethyl-benzylphosphonium	$[(C_2H_5)_3(C_7H_7)P]Br$.

ARSENIC-GROUP.

Monarsonium-salts. Ethyl-series.

Salt of Tetrethylarsonium	$[(C_2H_5)_4As]Br$.
Salt of Bromethyl-triethylarsonium	$[(C_2H_4Br)(C_2H_5)_3As]Br$.
Salt of Vinyl-triethylarsonium	$[(C_2H_3)(C_2H_5)_3As]Br$.

DIATOMIC-COMPOUNDS. PHOSPHORUS-GROUP.

Diphosphonium-salts.

Salt of Ethylene-hexethyldiphosphonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2$.
Salt of Ethylene-trimethyl-triethyl-diphosphonium	$\left[(C_2H_4)''\begin{matrix}(C\,H_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2$.
Salt of Ethylene-hexmethyldiphosphonium	$\left[(C_2H_4)''\begin{matrix}(C\,H_3)_3P\\(C\,H_3)_3P\end{matrix}\right]''Br_2$.

ARSENIC-GROUP.

Diarsonium-salts.

Salt of Ethylene-hexethyldiarsonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$.

PHOSPHORUS-NITROGEN-GROUP.

Phosphammonium-salts.

Salt of Ethylene-triethylphosphammonium	$\left[(C_2\,H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\quad N\end{matrix}\right]''Br_2$.
Salt of Ethylene-methyl-triethyl-phosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)H_2N\end{matrix}\right]''Br_2$.
Salt of Ethylene-tetrethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)H_2N\end{matrix}\right]''Br_2$.
Salt of Ethylene-pentethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Br_2$.
Salt of Ethylene-trimethyl-triethyl-phosphammonium	$\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3N\end{matrix}\right]''Br_2$.

PHOSPHORUS-ARSENIC-GROUP.

Phospharsonium-salts.

Salt of Ethylene-hexethylphospharsonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3As\end{matrix}\right]''Br_2$.

ARSENIC-NITROGEN-GROUP.

Arsammonium-salts.

Salt of Ethylene-triethylarsammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\H_3\quad N\end{matrix}\right]''Cl_2$.

The experiments described in the preceding pages refer almost exclusively to the study of compounds belonging either to the phosphorus-series or to the phosphorus-nitrogen-series. Numerous analogous terms of the nitrogen-series, monatomic as well as diatomic, with which I have become acquainted in the course of my researches, have been left unnoticed in this paper. I propose to examine the nitrogen-bodies in a special memoir; and I may here only remark, that these substances, although differing in several points, nevertheless so closely imitate, in their general deportment, the corresponding terms of the phosphorus-series, that the picture which in the preceding pages I have endeavoured to delineate of the phosphorus-compounds, illustrates, in a great measure, the deportment of the nitrogen-bodies. We meet here with the peculiar case of the study of the phosphorus-group being in advance of that of the nitrogen-series, whilst generally the investigation of the phosphorus-compounds was taken in hand only after inquiries in the nitrogen-series had furnished the prototypes to be copied.

In conclusion, a few words about the further development of which the experiments described appear to be capable, and about the direction in which I propose to pursue the opened track.

Conceived in its simplest form, the transition from the series of monatomic to that of diatomic bases may be referred to the introduction of a monochlorinated or monobrominated alcohol-radical into the ammonium-nucleus, the chlorine or bromine thus inserted furnishing the point of attack for a second molecule of ammonia. If in bromide of ethylammonium we imagine 1 equiv. of hydrogen in ethyl replaced by bromine, we arrive at the bromide of bromethyl-ammonium, which is capable of fixing a second molecule of ammonia, and of being thus converted into the dibromide of ethylene-diammonium, the latent bromine becoming accessible to silver-salts:

$$[(C_2H_4Br)H_3N]Br + H_3N = [(C_2H_4)'' H_6N_2]'' Br_2.$$

The further elaboration of this reaction suggests two different methods for the construction of polyatomic bases of a higher order. In the first place, the number of ammonia-molecules to be incorporated in the new system may be increased by the gradually advancing bromination of the radical. By the further bromination of ethyl in bromide of bromethyl-ammonium and the action of ammonia on the bodies thus produced, the following compounds might be generated:—

$$\begin{aligned}
[(C_2H_3Br_2)H_3N]Br + 2H_3N &= [(C_2H_3)''' \ H_9N_3]''' \ Br_3.\\
[(C_2H_2Br_3)H_3N]Br + 3H_3N &= [(C_2H_2)'''' \ H_{12}N_4]'''' \ Br_4.\\
[(C_2H\,Br_4)H_3N]Br + 4H_3N &= [(C_2H)''''' \ H_{15}N_5]''''' \ Br_5.\\
[(C_2Br_5) \ H_3N]Br + 5H_3N &= [(C_2)'''''' \ H_{18}N_6]'''''' \ Br_6.
\end{aligned}$$

Again the fixation of the ammonia-molecules might be attempted, not by the progressive bromination of the ethyl, but by the accumulation of monobrominated ethyl-radicals in the ammonium-nucleus. The bromide of the di-bromethylammonium, when submitted to the action of ammonia, would thus yield the tribromide of a triammonium, the bromide of tri-bromethylammonium, the tetrabromide of a tetrammonium; and, lastly, the bromide of tetra-bromethylammonium, the pentabromide of a pentammonium.

$$\begin{aligned}
[(C_2H_4Br)_2H_2N]Br + 2H_3N &= [(C_2H_4)_2{}'' H_8 N_3]''' \; Br_3.\\
[(C_2H_4Br)_3H\;N]Br + 3H_3N &= [(C_2H_4)_3{}'' H_{10}N_4]'''' \; Br_4.\\
[(C_2H_4Br)_4\quad N]Br + 4H_3N &= [(C_2H_4)_4{}'' H_{12}N_5]''''' \; Br_5.
\end{aligned}$$

As yet the bromination of the alcohol-bases presents some difficulty; appropriately selected reactions, however, will doubtless furnish these bodies. They will probably be obtained by indirect means, similar to those by which, years ago, I succeeded in preparing the chlorinated and brominated derivatives of phenylamine; or these substances may be generated by the action of pentachloride and pentabromide of phosphorus upon the oxethylated bases, a process which, from the few experiments recorded in this memoir, promises a rich harvest of results.

I have but faint hope that I may be able to trace these new paths to their goal; inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium- and tetrammonium-compounds begin to unfold themselves in unexpected variety.

I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus-bases. The truly philosophical spirit in which this talented chemist has accompanied me throughout the varying fortunes of this inquiry, will always be one of my most pleasing recollections.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 17th, 1861.

Alfred Smee, Esq., Vice-President, in the Chair.

James Apjohn, M.D., Professor of Chemistry, Trinity College, Dublin, was elected a Fellow of the Society; and Arthur Reynolds, Esq., Royal Arsenal Laboratory, Woolwich, was elected an Associate of the Society.

The following papers were read:—

"Analysis of the Saline Water of Purton, near Swindon," by Dr. Noad, F.R.S.

"On the Composition of Purton Water," by Dr. Voelker.

"On the Electrolytic test for Arsenic," by Professor Bloxam.

"On a new Silver-phosphonium-compound," by Dr. Hofmann, F.R.S.

February 7, 1861.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

John Davis, Esq., 20, Princes-street, Spitalfields; Charles Edward Beadnell, Esq., West Green-road, Tottenham.

The following were elected Associates of the Society:—

Dr. Charles Ulrich, 40, London-street: Edouard Louis Barrett, St. Bartholomew's Hospital.

The following papers were read:—

"On the Carbonates of Copper, Cobalt, and Nickel," by Mr. Frederick Field.

"On the Oxidation of Benzol," by Mr. A. H. Church.

February 21, 1861.

Dr. Warren De la Rue, Treasurer, in the Chair.

The following were elected Fellows of the Society:—

James Napier, Junior, Esq., 5, New Broad-street Buildings; William Weston, Esq., Museum of Practical Geology; Dr. Murray Thomson, Lecturer on Chemistry, Glasgow.

The following papers were read:—

"On the action of dilute Nitric Acid upon some Hydrocarbons of the Benzol series," by Warren de la Rue, M.D., and H. Müller.

"On the Putrefaction of Bile, and Formation of Gall-stones," by Dr. Thudichum.

"On the Bisulphide of Iodine," by Dr. Guthrie.

"On Ground Ice," by Mr. R. Adie.

March 7, 1861.

Dr. Hofmann, Foreign Secretary, in the Chair.

J. J. Coleman, Esq., Commercial College, Halifax, was elected a Fellow of the Society.

A paper was read,—

"On some Minerals from Chile," by Mr. Frederick Field.

Dr. Hofmann, made a verbal communication "On Mr. Griess's further researches upon Nitrogen-substitutions."

March 21, 1861.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

William Vazie Simons, Esq., 10, Avenue-road, Hammersmith; Edwin Burton Brown, M.D., Medical College, Lahore; Henry Owen Huskisson, Esq., 30, Mecklenburgh-square; Adam Clarke McLean, B.A., Wesleyan College, Taunton.

Professor Williamson delivered a discourse "On Thermodynamics in relation to Chemical Affinity."

Anniversary Meeting, March 30, 1861.

Professor Brodie, President, in the Chair.

The following Report of the Council, and the Audited Account of the Treasurer, were read:—

It is the custom at the Annual Meeting to lay before the Society a brief statement as to its progress.

The number of Fellows at the last annual meeting was 323; during the past year there has been an increase of 19, making the present number 342. The number of Associates is at present 10, being 2 less than the number of last year.

The increase of the Fellows of the Chemical Society is, to some extent, a measure of the interest felt in this country in the Science of Chemistry, and of the number of its cultivators. We may, therefore, observe with gratification, that the number of Fellows of our Society is steadily on the increase. Comparing the progress of the Society for the last 5 years, we find that from the year 1845 to 1850, the Society increased by 24 members, or 4·8 annually; from 1850 to 1856 (a period of 6 years) there was an increase of 35 members, or 5·8 annually; while from 1856 to 1861, there has been an increase of 86 members, or 17·4 annually, the rate of increase in the five years from 1856 to 1861 being more than three times and a-half as great as in the five years from 1845 to 1850.

Our Librarian, Mr. Watts, whose appointment was announced at the last Anniversary Meeting, has prepared a new Catalogue of the Society's Books. The Council is indebted to him for the promptitude and care with which he has produced this work, which, it is hoped, will tend materially to enhance the usefulness of the library.

The last year has happily not been marked by the loss of any eminent Chemist, either among the Fellows or Foreign Members. We have, however, to record the death of three of our Fellows, Mr. Charles Cowper, Mr. J. Macfarlane, and Mr. David Oldfield. A brief notice of two of these gentlemen will not be out of place.

Mr. J. F. Macfarlane had attained the Diploma of the Royal College of Surgeons of Edinburgh, and in early life practised for a short period; but he soon devoted himself to the business of a manufacturing Chemist and Druggist, which he carried on in Edinburgh, where he acquired considerable reputation as a manufacturer of the alkaloids and of chloroform. In 1818, he entered the Royal Medical Society of Edinburgh; was elected one of its Presidents in 1822, and in 1850 had the distinction of Honorary Member conferred upon him. He also, during a period of forty years, took an active interest in public matters, and was engaged in many important movements for the political and social benefit of his fellow-citizens.

Charles Cowper, one of our original Members, died on the 23rd December, 1860; he was born in London, on the 8th August, 1821. He was the son of the late Professor Cowper, of King's College, London (the Inventor of the printing machine now in common use) and brother of Mr. E. A. Cowper, Civil Engineer. Mr. C. Cowper studied Chemistry from early youth, under Dr. Faraday, Mr. Brande, and more practically under Mr. William Maughan; he was engaged as Practical Chemist with Messrs. Chance & Co., the large Glass Manufacturers, of Smethwick, near Birmingham, at whose works he made several useful improvements in the mixtures for coloured glass best adapted for Horticultural purposes, and in the working of sulphuric acid chambers, &c. He commenced business on his own account in London, as a Patent Agent, in 1848, and having had continual opportunities of observing and studying Engineering, he soon established a considerable reputation as a Patent Agent, both as regarded Chemical and Mechanical Inventions; and, owing to his careful attention to his profession, no Patent that he had specified, was ever lost.

He was much respected by a wide circle of friends, for his uprightness of character and great moral worth, added to a very amiable disposition.

List of Papers read at the Meetings of the Chemical Society, from March, 1860, to March, 1861:—

1. "On the Artificial Production of Tartaric Acid:" by Messrs. Perkin and Duppa.
2. "On Crystallized Potassium and Sodium:" by Mr. C. E. Long.
3. "On the History of Cinnamic Acid:" by Mr. D. Howard.
4. "On the Action of Sodium on Iodide of Methyl:" by Messrs. Wanklyn and Buckheisen.
5. "On Zinc-methyl:" by Mr. J. A. Wanklyn.
6. "On the Stibethyls and Stibmethyls:" by Mr. G. B. Buckton.
7. "On some Derivatives of the Olefines:" by Dr. Guthrie.
8. "On Baudrimont's Protosulphide of Carbon:" by Dr. Lyon Playfair.
9. "On the Composition of Hydrated Acids of constant boiling point:" by Dr. H. E. Roscoe.
10. "On Acetoxybenzamic Acid, an Isomer of Hippuric Acid:" by G. C. Foster, Esq.
11. "On the discrepancies in the statements of Pelouze and F. Mohr, respecting the solubility of Gallotannic Acid in Ether:" by Professor Bolley.
12. "On a hitherto unobserved source of Paraffin:" by Professor Bolley.

13. "On the Crystalline form of Metallic Chromium:" by Professor Bolley.
14. "On the Colouring Matter of Persian Berries:" by Professor Bolley.
15. "On the Basic Carbonates of Copper:" by Mr. F. Field.
16. "On the Separation of Volatile Ethyl-alkaloids:" by Dr. Hofmann.
17. "On a new Lead-salt corresponding to Cobalt-yellow:" by Mr. S. D. Hayes.
18. "On the production of mixed Amines, Phosphines, and Arsines:" by Dr. Hofmann.
19. "On the Laws of Gas-absorption:" by Mr. J. H. Sims.
20. "On Sugar in Urine:" by Dr. H. Bence Jones.
21. "On the Separation of Tellurium from Selenium and Sulphur:" by Dr. Oppenheim.
22. "On Nitroprusside of Sodium as a Re-agent:" by Dr. Oppenheim.
23. "Analysis of the Saline-water of Purton, near Swindon:" by Dr. Noad.
24. "On the Composition of Purton Water:" by Dr. Voelker.
25. "On the Electrolytic test for Arsenic:" by Professor Bloxam.
26. "On a new Silver-phosphonium-compound:" by Dr. Hofmann.
27. "On the Carbonates of Copper, Cobalt, and Nickel:" by Mr. F. Field.
28. "On the Oxidation of Benzol:" by Mr. A. H. Church.
29. "On the Action of Dilute Nitric Acid upon some Hydrocarbons of the Benzol series:" by Drs. De la Rue and Müller.
30. "On the Putrefaction of Bile and Formation of Gall-stones:" by Dr. Thudichum.
31. "On the Bisulphide of Iodine:" by Dr. Guthrie.
32. "On Ground Ice:" by Mr. R. Adie.
33. "On some Minerals from Chile:" by Mr. F. Field.

List of Discources delivered at the Meetings of the Chemical Society:—

"On Ozone:" by Dr. Thomas Andrews.

"On Circular Polarization:" by Dr J. H. Gladstone.

"On Organo-metallic Bodies:" by Dr. Frankland.

"On Thermo-dynamics in relation to Chemical Affinity:" by Dr. Williamson.

The following Report of the financial state of the the Society was read by the Treasurer:—

Drs. **THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.** Crs.

		£	s.	d.	£	s.	d.
1860. March 26.	To Cash in hand				565	3	3
July.	,, Half-yearly Dividend on £450 3 per cent. Consols				6	9	5
1861. January.	,, Half-yearly Dividend on £500 3 per cent. ,,				7	3	9
	,, Sundry Receipts from 25th March, 1860, to 25th March, 1861, as below:—						
	Life Compositions	70	0	0			
	Admission Fees	42	0	0			
	Resident Members' Subscriptions previous to 1860	20	0	0			
	Non-resident Members' Subscriptions previous to 1860	10	0	0			
	Resident Members' Subscriptions for 1860	60	0	0			
	Non-resident Members' Subscriptions for 1860	37	0	0			
	Resident Members' Subscriptions for 1861	234	0	0			
	Non-Resident Members' Subscriptions for 1861	96	0	0	569	0	0
					£1147	16	5

Assets	£	s.	d.
Balance in Cash	569	11	10
Invested in 3 per Cent. Consols	500	0	0
	£1069	11	10

		£	s.	d.	£	s.	d.
1860. Journal.	By Editor's Salary to 25th March, 1860	18	15	0			
	,, ,, ,, 25th ,, 1861	75	0	0			
	,, Editorial Expenses	1	6	0			
	,, Printing Journal	199	2	2	294	3	2
	,, Proceedings of Royal Society	..	..	..	20	0	0
Library.	,, Librarian's Salary to 25th March, 1860	6	5	0			
	,, ,, ,, ,, ,, 1861	25	0	0			
	,, Books and Magazines	6	7	0			
	,, Bookbinding	30	11	8			
	,, Spectrum Chart	0	5	0			
	,, Subscription to Cavendish Society	1	1	0	69	9	8
Collector and Clerk.	,, Collector's Commission	28	9	0			
	,, Clerk	3	0	0	31	9	0
	General Printing, Stationery, and Postages:—						
	By Harrison and Co.'s Account from July, 1858	29	17	6			
	,, Other Accounts, &c.	12	5	9			
	,, Carriage of Books, Postages, &c. (Hux's Book)	2	18	6	45	1	9
	Attendance, Coals, Gas, &c.:—						
	By T. Hux, Attendance from Michaelmas, 1860, to 1861	20	0	0			
	,, ,, (as per Book) Coals and Wood	1	8	0			
	,, ,, ,, Gas and Oil	2	6	9			
	,, Mr. and Mrs. Page, Lighting Fires	3	3	0			
	,, Gate Porter	1	1	0	27	18	9
	,, Royal Society, Share of Expenses for Refreshments	..	..	..	17	4	6
					505	6	10
Furniture.	,, Book Case (T. Fox)	24	10	0			
	,, Furniture (Hux's Book)	1	9	0	25	19	0
June 26.	By Purchase of £50 3 per cent. Consols	..	..	..	46	18	9
					578	4	7
	,, Balance at Coutts'	517	14	2			
	,, ,, in Cash	51	17	8	569	11	10
	£				1147	16	5

Examined and found correct,

AUGUSTUS MATTHIESSEN,
CHARLES HEISCH,
DANIEL HANBURY, } *Auditors.*

London, 20th March, 1861.

The following gentlemen were elected as Council and Officers for the ensuing year:—

President.—Dr. A. W. Hofmann.

Vice-Presidents who have filled the office of President.—W. T. Brande, B. C. Brodie, Dr. C. G. B. Daubeny, Thomas Graham, Dr. A. W. Miller, Dr. Lyon Playfair, Col. Philip Yorke.

Vice-Presidents.—Dr. H. Bence Jones, Robert Porrett, Alfred Smee, Dr. A. W. Williamson.

Secretaries.—T. Redwood, W. Odling.

Foreign Secretary.—Dr. E. Frankland.

Treasurer.—Dr. Warren De la Rue.

Other Members of Council.—Dr. Thomas Andrews, Dr. William Francis, Dr. J. H. Gladstone, Dr. G. D. Longstaff, Dr. Marcet, Dr. Normandy, W. H. Perkin, Dr. H. E. Roscoe, Dr. Edward Schunck, Dr. John Stenhouse, Robert Warington.

The thanks of the meeting were voted to the President, Officers, and Council, for their services to the Society; also to the Auditors and to the Scrutators.

April 4th, 1861.

Robert Warington, Esq., in the chair.

The following were elected Fellows of the Society:—

Frederick Norrington, Esq., 9, Charles-place, Plymouth; Robert Collyer, Ph.D., 8, Alpha-road, Regent's-park; Thomas Wood, Ph.D., 123, Upper Thames-street; Rev. John Henn, B.A., Greenhays, Manchester.

The following was elected an Associate of the Society:—

Mr. John Hall Smith, St. Mary's Hospital.

The following paper was read:—

"On some Derivatives from the Olefines:" by Dr. Frederick Guthrie.

April 18th, 1861.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Henry K. Bamber, Esq., Cheyne-walk, Chelsea; Arthur Ernest Sansom, M.B., 70, Brook-street, and Park-lodge, Fulham.

By a vote of the meeting, passed in accordance with the Byelaws, the following names were removed from the list of Fellows:—

A. G. Anderson, Benjamin Cooper, C. F. O. Glassford, C. R. James, J. E. Mayer, J. W. Perkins, Professor Pohl, Professor John Wilson.

Mr. Abel delivered a discourse—"On the Application of Electricity to the Explosion of Gunpowder."

May 2nd, 1861.

Robert Warington, Esq., in the chair.

Thomas Griffiths, Esq., 6, Stonefield-street, Lonsdale-square, N., was elected a Fellow of the Society:—

The following papers were read:—

"On the Action of Dibromide of Ethylene on Pyridine:" by Mr. J. Davidson.

"On the amount of Water displaced from the Hydrates of Potash, Soda, and Baryta, by Boracic and Silicic Acids:" by Professor Bloxam.

"On the Graphite of Cast-iron:" by Professor Crace Calvert.

May 16th, 1861.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Joseph Prestwich, Esq., F.R.S., Regent's-park; Thomas Lindsay, Esq., Millbank Brewery, Millwall; Edward Arnold, Esq., Norwich; Edward Cort Wright, Esq., 46, Mosley-street, Manchester.

Mr. W. H. Perkin delivered a discourse—"On the Colouring Matters obtained from Coal-tar."

June 6th, 1861.

Dr. Hofmann, President, in the chair.

The following papers were read:—

"On Bromide of Carbon:" by Mr. A. E. W. Lennox.

"On the power ascribed to the Roots of Plants of rejecting Poisons, or other Abnormal Substances presented to them:" by Dr. Daubeny.

June 20th, 1861.

Dr. Warren De La Rue, Treasurer, in the chair.

The following were elected Fellows of the Society:—

Dr. John Dauglish, Reading; Henry Curwen Salmon, F.G.S., 36, Lemon-street, Truro; W. H. Harris, Esq., 33, Gold-street, Northampton.

The following paper was read:—

"On the Constitution of Gastric Juice:" by Dr. Marcet.

A discourse was delivered by Dr. H. E. Roscoe—"On the Application of the Induction-coil to Steinheil's Apparatus for Spectrum analysis."

November 7th, 1861.

Dr. Hofmann, President, in the chair.

The following papers were read:—

"On the Action of certain Gases upon the Peroxides of Potassium and Sodium:" by A. Vernon Harcourt, Esq.

"On some results of the Analyses of Commercial Copper:" by Messrs. Abel and Field.

"On the occurrence of Bismuth in various descriptions of Copper ore:" by Mr. F. Field.

November 21st, 1861.

Dr. Hofmann, President, in the chair.

Peter McOwen, B.A., Huddersfield College, was elected a Fellow of the Society.

The following papers were read:—

"On Leucic Acid and some of its Salts:" by Dr. Thudichum.

"On the occurrence of Crystalline Deposits of Phosphate of Lime in human Urine:" by Dr. H. Bence Jones.

"On Sparteine:" by Mr. E. J. Mills.

December 5th, 1861.

Dr. Miller, Vice-President, in the chair.

The following papers were read:—

"On Peppermint-camphor:" by Dr. Oppenheim.

"On Piperic and Hydro-piperic Acids:" by G. C. Foster, B.A.

"On Supplementary Experiments upon the power ascribed to the Roots of Plants of rejecting Poisons and Abnormal Substances presented to them:" by Dr. Daubeny.

"On some Physical Properties of Tin-lead Alloys:" by Professor Bolley.

"On the Dangers arising from the use of certain Waters for feeding Steam-boilers:" by Professor Bolley.

Donations to the library received in the year 1861:—

"On Coal, Petroleum, and other distilled Oils;" by A. Gessner: from the Author.

"On the Origin of Species by means of Organic Affinity;" by H. Freke: from the Author.

"Memorials of Dr. Priestley;" by James Yates: from the Author.

"Report of Experiments on the Growth of Red Clover;" by J. B. Lawes, F.R.S., and J. H. Gilbert, Ph. D., F.R.S.: from the Authors.

"On the Sources of the Nitrogen of Vegetation;" by J. B. Lawes, F.R.S., J. H. Gilbert, Ph.D., F.R.S., and Evan Pugh, Ph.D., F.C.S.: from the Authors.

"On the Solubility of Bone-earth from various Sources in

Solutions of Chloride of Ammonium and Common Salt;" by James Birney: from the Author.

"Composition of Linseed and Rape Cakes, which are now selling (1859) in the Dublin Market; and the Composition of Artificial Cattle-food;" by James Birney and John McDowell: from the Authors.

"On the Separation of Copper and Iron by means of Ammonia, and the Analysis of some Irish Copper Ores;" by Edward Byrne: from the Author.

"On the Valuation of Soils and the Nutrition of Plants;" by Robert Galloway: from the Author.

"Investigations conducted at the Laboratory of the Museum of Irish Industry," (1858 to 1859): from the Directors.

"A Notice of the Origin, Progress, and Present Condition of the Academy of Natural Sciences of Philadelphia," (1860): by W. S. W. Raschenberger, M.D.: from the Academy.

"Contributions to the History of the Phosphorus-bases;" by A. W. Hofmann, Ph.D., F.R.S.: from the Author.

"On the Relation between Boiling Point and Composition in Organic Compounds;" by Dr. H. Kopp: from the Author.

"On the Conductibility of Mercury and Amalgams;" by Messrs. Calvert and Johnson: from the Authors.

"On the Expansion of Metals and Alloys;" by Messrs. Calvert and Johnson: from the Authors.

"Manual of Chemistry; Descriptive, Theoretical, and Practical;" by William Odling, M.B., F.R.S.: from the Author.

"Report on the Explosion of Gunpowder by Electricity;" by Messrs. Wheatstone and Abel: from the War Office.

"On the Chromate of Chromium and Analogous Chromates;" by F. H. Storer and C. W. Elliot: from the Authors.

On the Constitution of Anthracene or Paranaphthalin;" by T. Anderson: from the Author.

"Second Report of a Geological Reconnaissance of the Southern and Middle Counties of Arkansas:" from the Smithsonian Institution at Washington.

"Review of Dr. Antisell's Work on Photogenic Oils;" by F. H. Storer: from the Author.

"Traité de Chimie Générale Elémentaire;" par A. Cahours, 2me Edition, 3 tomes: from the Author.

"Histoire des Radicaux Organiques;" par A. Cahours: from the Author.

"Dictionnaire de Chimie Industrielle;" par MM. Barreswil et Girard, Introduction et Tome premier: from the Authors.

"Sur quelques Phenomènes Météorologiques sur le litoral de la Flandre occidentale," par T. L. Phipson.

"Sur une nouvelle Roche de formation recente sur le litoral de la Flandre occidentale," par T. L. Phipson.

"La Force catalytique, ou Etudes sur les Phenomènes de Contact," par T. L. Phipson.

"Sur une Matière colorante extracte du *Rhamnus Frangula,*" par T. L. Phipson.

"Sur les Bolets bleuissants; Etudes de formation des Principes colorants chez plusieurs Champignons," par T. L. Phipson.

"Mémoire sur la Fécule et les substances qui peuvent la remplacer dans l'Industrie," par T. L. Phipson.

"Recherches nouvelles sur le Phosphore," par T. L. Phipson.

"Sur la Phosphorescence en générale, et sur les Insectes phosphoriques en particulier," par T. L. Phipson:
from the Author.

"Handbuch der technisch-chemischen Untersuchungen," von Dr. P. A. Bolley: from the Author.

"Ueber königliche Massnahmen für das Gedeihen der Wissenschaften," von F. von Thiersch: from the Royal Bavarian Academy of Sciences.

"Das chemische Laboratorium der Universität Christiania, und die darin ausgeführten chemischen Untersuchungen;" herausgegeben, von Adolph Strecker, Director des Laboratoriums: from the University of Norway.

Periodicals:—

"Philosophical Transactions," 1860, Pt. I.: from the Royal Society.

"Transactions of the Royal Society of Edinburgh," Vol. XXII., Pt. II.

"Appendix to the Makerstoun Magnetical and Meteorological Observations," being a Supplement to Vol. XXII of the Transactions of the Royal Society of Edinburgh.

"Proceedings of the Royal Society of Edinburgh," Session 1859 to 1860: from the Royal Society of Edinburgh.

"Memoirs of the Royal Astronomical Society," Vol. XXIX.

"Monthly Notices of the Royal Astronomical Society," from Dec. 1860, to Dec. 1861: from the Society.

"Quarterly Journal of the Geological Society for 1861:" from the Society.

"Notices of the Proceedings of the Members of the Royal Institution of Great Britain," Part 11 (1860–61).

"List of Members, Officers, &c., of the Royal Institution," 1861.

"Additions to the Library of the Royal Institution," from July 1860 to July 1861:

From the Royal Institution.

"Journal of the Photographic Society," for 1861: from the Society.

"Pharmaceutical Journal," for 1861: from the Editor.

"Journal of the Society of Arts," No. 422 to 472: from the Society.

"Chemical News," No. 55 to 69: from the Editor.

"Literary Gazette," No. 130 to 176: from the Editor.

"London Review," No. 31 to 73: from the Editor.

"The British Journal Photographic Almanac," for 1861: from the Editor.

"Calendar for the year 1861, of the Science and Art Department of the Committee of Council on Education:" from the Department.

"Twenty-eighth Report of the Royal Cornwall Polytechnic Society:" from the Society.

"Annual Report of the Yorkshire Philosophical Society," 1860: from the Society.

"Proceedings of the Royal Society of Liverpool" (1860–61): from the Society.

"Smithsonian Contributions to Knowledge," Vols. XI, XII.

"Smithsonian Reports," for 1859:

from the Smithsonian Institution at Washington.

"American Journal of Science and Arts," for 1861: from the Editor.

"Journal of the Franklin Institute," for 1861: from the Institute.

"Proceedings of the Academy of Natural Sciences of Philadelphia," for 1860, pp. 285 to 579, 1861, No. 1—4: from the Academy.

"Proceedings of the American Philosophical Society," Vol. VII, No. 63: from the Society.

"Annual Report of the Cooper Union of Sciences and Art," for 1860: from the Union.

"Canadian Journal:" from the Canadian Institute.

"Canadian Naturalist and Geologist," Vol. VI, No. 1—to 4: from the Natural History Society of Montreal.

"Bulletin de la Société d'Encouragement pour l'Industrie Nationale," No. 94—105: from the Society.

"Bulletin de la Classe des Sciences de l'Académie Royale de Belgique," 1860.

"Annuaire de l'Académie Royale de Belgique, 1861: from the Academy.

"Mélanges Physiques et Chimiques," Tome IV., Livraisons 1—5: from the Imperial Academy of Sciences at St. Petersburgh.

"Denkschriften der kaiserlichen Akademie der Wissenschaften zu Wien:" Band XIX.

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften zu Wien:" Band XLI, Nos. 13—20; Band XLII, Nos. 21—28; Band XLIII, 1.

"Jahrbuch der konigl.-kaiserlichen Central-Anstalt für Meteorologie and Erdmagnetismus," von Karl Kreil, 1855: from the Imperial Academy of Sciences at Vienna.

"Sitzungsberichte der königlich-baeyerischen Akademie der Wissenschaften zu München," 1860, Hefte 4—5; 1861. Hefte 1—4: from the Royal Bavarian Academy.

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